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**PROCEEDINGS**  
**OF**  
**THE SYMPOSIUM**  
**ON**  
**ROLE OF PHOSPHATES IN THE SOIL,**  
**PLANT AND ANIMAL KINGDOM**  
**PART I**

**NATIONAL ACADEMY OF SCIENCES, INDIA**  
**ALLAHABAD**

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# PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA 1956

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PART IV

## PRESIDENTIAL ADDRESS

### **CALCIUM PHOSPHATES AND THEIR IMPORTANCE IN NITROGEN FIXATION AND ALKALI SOIL RECLAMATION**

*By*

PROF. N. R. DHAR

*(Sheila Dhar Institute of Soil Science, University of Allahabad)*

Since the discovery of phosphorus, perhaps independently, by Brandt, Kunckel and Boyle about 300 years ago, phosphorus and its compounds have been intensively studied by physicists, chemists, agronomists and biologists because of the importance of this element and its compounds in industry, agriculture and in all living beings.

In recent years it has been established by the Academies of Sciences, Medicine and Agriculture of France that during the German occupation of France in the last world war, not only the fertility of the French soils badly suffered due to the want of phosphorus but the health of animals and human beings also was adversely affected due to the same reason.

It is well known that all animal bones consist chiefly of tricalcium phosphate. Hence, an adequate supply of available phosphate and calcium is indispensable for maintenance of health.

All micro-organisms flourish in presence of an adequate dose of phosphate. All plants must have phosphate which is an integral part of all plant tissues.

In biological reactions phosphorus is of the utmost importance since it is essential for life. Phosphorus occurs in cytoplasm and in bones, teeth, shells and other parts of animals. Plants must contain phosphates which are derived from soils the fertility of which is determined by their phosphate contents. The phosphate contents of the skeletal remains of some species of animals are recorded below :—

Mammals.....	18.55 %
Birds.....	18.01 %
Fishes.....	18.46 %
Reptiles.....	16.98 %
Amphibia.....	16.27 %

In this connection it is interesting to record that the inorganic phosphorus content of normal human serum from birth to 20 years remains remarkably constant at 5.6 mgms. per hundred c. c. of serum. At 20 years of age the phosphorus content drops sharply to 3.75 mgms. and remains constant throughout adult life. During the period of union of fractures in adults, the phosphorus content of the serum should be raised to about the same level as in childhood.

In the following table the nitrogen, phosphorus and potash contents of some crops are recorded :—

#### NUTRIENT CONTENT OF SOME FIELD AND HORTICULTURAL CROPS

Crop	Yield	Part of crop		N (lbs.)	P (lbs.)	K (lbs.)	Totals
Cotton	500 lbs.	Lint	...	38	8	12	58
	1,000 lbs.	seed	...				
	1,500 lbs.	burrs, leaves, stalks	...	27	3	30	60
		Total	...	65	11	42	118
Tobacco	1,500 lbs.	Leaves	...	55	4	66	125
		stalks	...	25	4	29	58
		Total	...	80	8	95	183
			...				
Corn	60 bu.	Grain	...	57	10	12	79
	2 tons	Stover	...	38	5	46	89
		Total	...	95	15	58	168
			...				
Wheat	30 bu.	Grain	...	35	7	7	49
	1.25 tons.	Straw	...	15	2	17	34
		Total	...	50	9	24	83
			...				
Oats	50 bu.	Grain	...	35	6	8	49
	1.25 tons.	Straw	...	15	2	29	46
		Total	...	50	8	37	95
			...				
Barley	40 bu.	Grain	...	35	6	8	49
	1 ton.	Straw	...	15	2	24	41
		Total	...	50	8	32	90
			...				
Potatoes	300 bu.	Tubers	...	65	11	95	171
		Tops	...	60	4	46	110
		Total	...	125	15	141	281
			...				
Sweet potatoes	300 bu.	Roots	...	45	6	63	114
		Wines	...	30	2	33	65
		Total	...	75	8	96	179
			...				
Sugar beets	15 tons.	Roots	...	55	10	44	109
		Tops	...	60	10	76	146
		Total	...	115	20	120	255
			...				
Tomatoes	10 tons.	Fruit	...	60	9	66	135
		Vines	...	40	6	79	125
		Total	...	100	15	145	260
			...				



Crop	Yield	Part of crop		N (lbs.)	P (lbs.)	K (lbs.)	Totals
Cabbage	15 tons.	All	...	100	11	83	194
Celery	350 crates.	All	...	80	21	195	296
Spinach	9 tons. or 1,000 bu.	All	...	90	13	37	140
Apples	400 bu.	Fruit	...	20	3	25	48
		Leaves, wood	...	10	2	4	16
		Total	...	30	5	29	64
Peaches	500 bu.	Fruit	...	30	6	46	82
		Leaves, wood	...	55	4	37	96
		Total	...	85	10	83	178
Grapes	4 tons.	Fruit	...	10	3	17	30
		Leaves, canes	...	15	2	1	18
		Total	...	25	5	18	48
Oranges	600 boxes	Fruit	...	65	10	87	162
		Leaves, wood	...	25	3	20	48
		Total	...	90	13	107	210
Soybeans	25 bu. 1.25 tons.	Grain	...	110	15	33	158
		Straw	...	15	2	17	34
		Total	...	125	17	50	192
Peanuts	1 ton 3 tons	Nuts	...	60	4	8	72
		Vines	...	25	2	33	60
		Total	...	85	6	41	132
Pea beans	30 bu.	Grain	...	73	10	20	103
		Straw	...	22	3	26	51
		Total	...	95	13	46	154
Alfalfa	3 tons	All	...	140	15	112	267
Sweet clover	5 tons	All	...	185	20	137	342
Red clover	2 tons	All	...	80	9	58	147
Lespedeza	3 tons	All	...	130	13	58	201
Cowpeas	2 tons	All	...	125	10	75	210
Timothy	1.5 tons	All	...	40	6	37	83

*Conclusions* The foregoing results show clearly that the phosphate contents of crops are smaller than the nitrogen and potash contents.

Bacteria	...	...	15000 p.p.m.
Fungi	...	...	10000 p.p.m.
Algae	...	...	2000 p.p.m.
Bryophyta	...	...	1500 p.p.m.
Lichens	...	...	800 p.p.m.

It is interesting to note from the above results that the phosphorus contents of bacteria and fungi are high and, hence, in presence of soluble phosphates, they multiply readily. The following results show that the bark, needles and leaves of trees are good sources of  $P_2O_5$  (p.p.m. of dry matter) :—

		Pines	Spruce	Beech
<i>Root</i>				
	Wood ...	77	...	170
	Bark ...	330	...	220
<i>Trunk</i>				
	Wood ...	47	49	110
	Bark ...	300	350	650
<i>Branches</i>				
	Wood ...	240	...	220
	Bark ...	620	140	700
<i>Turges</i>				
	Wood ...	240	...	...
	Bark ...	620	...	700
	Needles, leaves ...	1100	1300	1300

In a foregoing paper, it has been stated that the ratio of Ca : P varies from 0.978 in oats to 3.63 in turnips. If we assume that the calcium and phosphate ions combine and form tricalcium phosphate in the plant system, the ratio of Ca : P should be 1.93. It is clear, therefore, that the whole of the calcium does not exist in the plant system as calcium phosphate but may combine with other acid-forming radicals. Similarly, the phosphate not only combines with calcium but may also combine with other bases.

It is of great interest to note that in wheat straw the ratio of Ca : P is 1.966, practically the same as in tricalcium phosphate, whilst in oat straw, the ratio is 2.5. When these materials, rich in  $P_2O_5$  are added to the soil, it is enriched by calcium phosphate.

It is well known that the percentage of calcium in the leaves of forest trees varies from 0.55 to 3.94% whilst that of phosphorus varies from 0.04 to 0.28%. The average of the ratio Ca : P of leaves of some American trees is 14 : 1. This is a very interesting fact that the phosphate content of the tree leaves in comparison to calcium is much smaller than in straw of wheat or oat. Similarly, the ashes of parts of trees have Ca : P ratio 28 : 1.

From intensive researches carried on in the Sheila Dhar Institute of Soil Science, University of Allahabad, we have discovered the following important roles played by phosphates in improving land fertility :—

- (1) Phosphates markedly check the leaching of lime.
- (2) Phosphates markedly increase the fixation of atmospheric nitrogen in soils by the oxidation of all types of organic matter which, at the

same time, increases the availability of added phosphates ; but ferric and aluminium phosphates are much inferior to calcium and magnesium phosphates.

- (3) In composting of all plant materials, specially those which are rich in lignin, finely powdered phosphate rock, basic slag, superphosphate and powdered bone have been found to increase the value of such composts by fixing atmospheric nitrogen and producing available phosphates. Hence, in composting of plant materials all over the world, calcium phosphate in any form is certainly profitable.
- (4) Calcium phosphates markedly retard the loss of nitrogen from soils on the addition of nitrogenous manures and fertilizers.
- (5) Moreover, we have discovered that a mixture of finely powdered basic slag or phosphate rocks and organic substances like straw, leaves, *sanaï* (Sann hemp), *dhaincha*, cow pea, molasses etc. is very effective in reclaiming alkaline lands permanently.

We are also studying the problem of phosphorylation of different carbohydrates and nitrogenous compounds and we are inclined to the view that phosphoric acid forms fairly stable complexes with these materials.

### WORLD PHOSPHATE RESOURCES AND THEIR ORIGIN

The ocean is a vast reservoir of phosphorus from which the largest deposits of calcium phosphates have been formed. The principal sources of phosphorus are the mineral phosphates, iron ore and bone. Phosphorus ranks 12th in order of abundance amongst the 95 or more chemical elements occurring on the earth's crust. All terrestrial matter contains 0.25%  $P_2O_5$ , 0.3% nitrogen and 2.89%  $K_2O$ .

It is well known that the natural phosphate deposits of the world can be broadly classified into three groups : (a) igneous or magmatic primary rocks, (b) sedimentary rocks believed to be derived from organic matter and (c) phosphates of iron and aluminium such as wavellite, amblyonite another aluminium phosphate. The element phosphorus is widely distributed in the earth's crust which contains 0.12% phosphate chiefly as calcium orthophosphate. Limestone often carries tricalcium phosphate varying from trace to 80%. Most natural soils in temperate countries are deficient in available phosphorus. But there are lands where the phosphate content is greater than the parent rock materials from which the soils have been formed. Soil organic matter in temperate climates is believed to contain 1/3rd of its phosphorus in the organic form. The phosphate mineral present in most world soils is crystallised tricalcium phosphate containing small amounts so calcium chloride and calcium fluoride. This primary igneous mineral is usually called apatite of which five varieties have been studied. The carbonatoapatite has the usual formula  $(Ca_3(PO_4)_2)_3 \cdot CaCO_3$  a fluor apatite whose chemical composition may be represented by the formula  $(Ca_3(PO_4)_2)_3 \cdot CaF_2$ , a chlorapatite having the formula  $(Ca_3(PO_4)_2)_3 \cdot CaCl_2$ , a hydroxyapatite having the formula  $(Ca_3(PO_4)_2)_3 \cdot Ca(OH)_2$  and a sulphatoapatite having the formula  $(Ca_3(PO_4)_2)_3 \cdot CaSO_4$ .

It is well known that tricalcium phosphate, calcium sulphate, calcium fluoride, are sparingly soluble in water and, hence, these apatites which are extremely aged being derived from the primary igneous rocks, are very sparingly soluble in water. Similarly, the natural rocks containing aluminium or ferric phosphate are almost insoluble in water. Hence, these apatites and the other

phosphatic minerals are not washed away much by rain water and are preserved in the soil.

Phosphoric acid has been detected in small quantities in rivers and spring water. For example in France, Department of Seine and Oise, a spring contains  $\text{PO}_4$  to the extent of over 20% of the total dissolved matter (1 litre contains 0.49 gr. almost 0.05%). Phytin, lecithin, nuclein etc. are animal and plant proteins containing P.

Vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) found in bogs and swamps; brushite ( $\text{Ca HPO}_4 \cdot 2\text{H}_2\text{O}$ ) newberyite ( $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ), struvite ( $\text{NH}_4 \text{ Mg } \text{PO}_4 \cdot 6 \text{ H}_2\text{O}$ ), chlorapatite ( $\text{Ca}_3(\text{PO}_4)_3 \text{ Cl}$ ), Fluor apatite  $\text{Ca}_3(\text{PO}_4)_3 \text{ F}$ , tripolite ( $\text{Mn Fe}_2 \text{ FPO}_4$ ), amblygonite  $\text{Li (Al, Fe) PO}_4$ , monazite ( $\text{Ce, La, Dy) PO}_4$ , xenotime  $\text{YPO}_4$ , pyromorphite  $\text{Pb}_5 \text{ Cl (PO}_4)_3$  are important phosphatic minerals etc. the latter are rare.

### SEA—A VAST SOURCE OF CALCIUM PHOSPHATE

The natural phosphate rocks in North Africa, U. S. A. and Oceania are residual, replacement or sedimentary type. In Tennessee, U. S. A., brown phosphate rocks occur and they are believed to be derived from phosphatic limestone. On the other hand, in Oceania, replacement phosphates occur in Nauru and Ocean Island. These are believed to be limestones which have been phosphatised and changed to calcium di phosphate and triphosphate by the action of guano or other organic sources of phosphates. The North African deposits which are next in importance to those in North America are believed to be sedimentary deposits obtained from the sea bottom. These are usually interbedded with limestones and shales. Such deposits existed on the floor of the sea. Sea water contains phosphates in small amounts as is shown in the following table :—

#### CONCENTRATIONS OF PHOSPHATE IN ATLANTIC WATERS.

*Micrograms per litre.*

Phosphorus as inorganic phosphate in solution.

##### ANTARCTIC :

Upper layers	...	...	...	62-64
Below 150 m.	...	...	...	75-85

##### NORTH ATLANTIC :

Upper 20-50 m.	...	...	...	often 1 in summer.
Below 600 m.	...	...	...	c. 40

##### ENGLISH CHANNEL :

Upper layers in summer	...	...	...	1-3
Winters maximum, varying from year to year	...	...	...	10-23

This phosphate is drawn upon by sea organisms. In the sea, not only orthophosphate but small amounts of dissolved organic phosphates are absorbed by phytoplankton.

It is generally believed by biologists that large amounts of organic phosphates are held in the cells of sea organisms. These organic forms of phosphate, on the decay of the organisms, undergo dephosphorylation with the production of ortho-

phosphate. Under natural conditions the phytoplankton is eaten by zooplankton and sea animals.

Phosphorus is essential for the growth of phytoplankton. At times, a lack of phosphate may limit the primary productivity of the sea.

The utilisation of phosphate and nitrate in the synthesis of organic substances proceeds at approximately parallel rates. The optimum concentration of phosphate-P for the development of diatoms is about 50 mgm/M<sup>3</sup> according to Harvey. Water, throughout the euphotic zone, rarely contains more than 5 mgm/M<sup>3</sup> during the photosynthetic season and generally less than 1 mgm/M<sup>3</sup>. At such times a majority of the total phosphorus content of water occurs in plant and animal tissues. Upon the death of the organisms, phosphate is rapidly regenerated.

It is well known that bacterial cell substance is notoriously rich in phosphorus. However, it is apparent from their minute size and small numbers that bacteria do not compete effectively for the sea's limited store of this element. There is no evidence that phosphate limits bacterial multiplication in sea water unless the latter is experimentally enriched with organic matter. Phosphorus occurs in organisms primarily in the form of phospholipids and nucleoproteins. Animal bones consist largely of tricalcium phosphate. Most organic phosphorus compounds seems to be very susceptible to decomposition by bacteria. Phosphate is liberated very early in the process. In experiments conducted by Seiwel and Seiwel in 1928, about half of the content of freshly collected zooplankton was decomposed in 24 hours after the death of the zooplankton whereas, oxygen consumption by bacteria in the experiments indicated that half of the total organic content of the zooplankton was not oxidised for 4 or 5 days. In similar experiments conducted by Cooper in 1935, about 1/4th to 1/3rd of the phosphorus content of marine zooplankton was liberated as phosphate during the first 12 hours of bacterial activity and nearly all of it in 6 days. Phosphate was liberated from phytoplankton somewhat less rapidly.

The occurrence of a far greater concentration of phosphate in deep water than near the surface has been interpreted by some oceanographers as indicating that phosphorus is regenerated in bottom deposits. The foregoing observations on the rapidity of phosphate regeneration together with other considerations strongly suggest that the majority of the phosphorus cycle is enacted in the euphotic zone. There large quantities of phosphate may be regenerated, but, phosphate may not accumulate because it is utilised by phytoplankton or bacteria almost as rapidly as it is regenerated.

Redfield believes that in the phosphate maximum and oxygen minimum in the North Atlantic regions, phosphate may be added and oxygen removed by the decomposition of sinking organic matter.

The solubility of phosphate in sea water is primarily a function of the pH. The solubility is increased as a result of the activities of the bacteria which produce acidic substances and it is decreased by metabolites of alkaline character. In localised microspheres where the phosphate content of the water is relatively high, tricalcium phosphate may be precipitated from solution owing to an increased pH caused by bacteria. The reverse process, namely, the dissolution of tricalcium phosphate, may be of considerable importance in the phosphorus cycle. It is of importance on land where bacterial activity promotes the mineralisation of rock phosphates. In the sea large quantities of phosphate are bound in the bones of animals in the form of tricalcium phosphate. Part of the latter may be dissolved

by the acidic digestive juices of carnivorous animals and part by bacteria and allied microorganisms. This they do in 4 different ways recorded in order of importance : (1) generation of acids, (2) decomposition of organic matter associated with the bones thereby mechanically liberating some calcium phosphate, particularly from only partially ossified tissues, (3) production of ammonium salts and other secondary reaction products which increase the solubility of tricalcium phosphate, but,  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$  have a slight solvent action and (4) conversion of insoluble tricalcium phosphate into cell phosphoproteins or phospholipids by direct assimilation.

Tricalcium phosphate, either in the form of bone or crystals, provides an excellent surface for the attachment of marine bacteria and for the concentration of dissolved organic matter. This would promote increased bacterial activity in the immediate vicinity of the tricalcium phosphate where bacteria in microspheres may produce enough acid to have a solvent action, though, surrounded by slightly alkaline water.

#### SOFT PHOSPHATED LIME STONES CONTAINING SMALL AMOUNTS OF FLUORINE SUITABLE FOR DIRECT APPLICATION

Guano is derived from a Spanish word meaning dung. Guano is usually the excrement of sea fowl, e. g. cormorants, pelicans and gannets. Sometimes, the excrements of turtles, seals together with bones and feathers of dead birds are mixed with guano.

Guano deposits are found in many parts of the world, but, usually, on islands. Only a few deposits have been located on the coast of main lands. The most valuable deposits are found on the islands of the Pacific ocean on the coast of Peru. The inhabitants of this country were acquainted with the fertilizing value of this material from a long time. The deposits of guano may be new or ancient and may be, sometimes, 200 feet thick. Where the climate is moist, fermentation takes place and the composition is considerably changed. The food of sea fowl is made up largely of fish. Hence, guano may consist of both—phosphate and nitrogenous compounds. The principal nitrogenous compound is uric acid in the excrements of birds, but, Peruvian guano does not contain uric acid which has undergone change into ammonium carbonate, sulphate and phosphate which are readily available to crops. If the guano has already been fermented and the nitrogenous compounds have undergone nitrification and nitrogen has been lost due to the formation and decomposition of the unstable substance, ammonium nitrite, the guano may contain 20 to 25%  $\text{P}_2\text{O}_5$  and only 4 to 6% nitrogen. The phosphate in guano is usually in the form of calcium or ammonium phosphate. On the other hand, in dry places such as Peru, the guano is richer in nitrogen and may contain 10 to 16% nitrogen, 8 to 12%  $\text{P}_2\text{O}_5$  and 2 to 3% potash.

When such a guano is dropped on calcareous soil or chalk deposits, double decomposition takes place, the soluble phosphates slowly react with calcium carbonate and form tricalcium and, perhaps, dicalcium phosphates. The nitric acid obtained from the nitrification of the nitrogenous compounds in guano makes the calcium carbonate soluble and may produce dicalcium phosphate  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . Consequently, the phosphate deposits in many islands as well as coastal regions of main lands may have originated by the action of guano on limestone or calcareous soils. Such deposits are likely to be poor in fluorine, because, the amount of fluorine in fish is exceedingly small. The Curacao phosphate in the Dutch island of Curacao off Venezuela contains the smallest amount of fluorine,

i. e. 0.38%. The amount of iron and aluminium oxide in this phosphate is also very small. The bulk of this phosphate which appears to be a gel when magnified to a limited extent is actually found on further examination to consist of micro-crystals possibly of dicalcium phosphate and tricalcium phosphate. Organic materials are associated with this phosphate. Christmas Island phosphate is similar in property to that of the Curacao phosphate. These are likely to be derived from the excrements of birds, i. e. essentially derived from the fish life in the ocean. It has been estimated by Murphy that a square mile of the territory occupied by the sea fowls on some of the Peruvian islands has supported 5600000 birds. A thousand or more tons of fish per day would be required for maintaining such a big colony of birds.

Apart from these phosphated limestones which are usually soft, there are other types of natural calcium phosphate which are derived from the deposits in the sea floor. These are derived from marine organisms as well as bones of sea animals, seals, fishes etc. On the death of these, the organic matter undergoes rapid transformation and the calcium phosphate becomes concentrated. Due to volcanic and other upheavals, the sea beds are raised above the surface of the sea and the calcium phosphate remains almost unchanged. As sea water contains appreciable quantities of fluorine, i. e. 1400 mgms. per cubic metre of sea water, the calcium phosphate obtained from the bottom of the sea is usually richer in fluorine than the phosphated limestones obtained from guano and other sources. It is interesting to record that there is more fluorine in sea water than phosphorus, because, it is stated that sea water contains approximately 30 mgms. of orthophosphate as phosphorus and 8 mgms. of phosphorus as organic phosphate per cubic metre of sea water which contains usually 1400 mgms. of fluorine as stated above. This explains why the natural phosphate derived from the sea bottom are richer in fluorine than the phosphated limestones discussed before.

It is generally believed that many of the deposits in North Africa and south-eastern part of the United States have originated from the deposits on the sea floor. Many bones and teeth of fish have been found in some of these deposits which are amorphous and show evidence of organic origin.

As the fluoride content usually determines the solubility of the sedimentary phosphate deposits there is no doubt that the phosphatised limestones which are poor in fluorine are usually more soluble in water than the phosphate rocks obtained from the bottom of the sea which are richer in fluorine. Consequently, for direct addition to the soil the phosphated limestones are better than the phosphate rocks obtained from the sea bottom richer in fluorine. This is a matter of great importance in permanent agriculture.

K. D. Jacob has reported that the fluorine <sup>contents</sup> of French Morocco, Tunisia, Christmas Island, Nauru, Island, Ocean Island, Curacao, Florida Land Pebble, Florida Hard Rock, Florida Waste Pond, Tennessee Brown Rock, Tennessee Blue Rock, South Carolina and Idaho, Montana and Wyoming rock phosphates are 4.24%, 3.46%, 1.51%, 2.7%, 3.08%, 0.74%, 3.3 to 4%, 3.4 to 3.9%, 2.0 to 2.2%, 3.2 to 3.9%, 3.3 to 3.8%, 3.3 to 3.7% and 3.1 to 6.9% (in case of the last 3) respectively.

In this connection the following lines are of importance :—

“Phosphorite or amorphous phosphate rock, which occurs in sedimentary deposits (usually of marine origin) in many parts of the world, is by far the most important of the raw materials used as sources of phosphoric acid for fertiliser and

other industrial purposes. Jacob found that nearly all deposits of phosphorite contain F and  $P_2O_5$  in the same ratio as they occur in apatite. The presence of fluorine as a constituent part of the calcium phosphate molecule is responsible for the low solubility of the  $P_2O_5$  and accounts for the accumulation and preservation of these phosphate deposits".

In Gray's book "Phosphates and Superphosphates", on pages 53-71, results of chemical analysis of various phosphate rocks are recorded. From these data it appears that Coprolites, Morocco phosphate (Khouribga and Safi), Safi (Morocco) phosphate, two samples of Gafsa (Tunis) phosphate, Kalaa Djerda (Tunis) phosphate, Dyr (Tunis) phosphate, Florida Hard Rock phosphate, various grades of Land Pebble phosphate, typical phosphate rocks of U. S. A., Ocean island phosphate, Nauru phosphate, Kola phosphate of U. S. S. R., Safaga (Egypt) phosphate, contain fluorides in greater amounts than 2%. On the other hand, Djebel M'Dilla (Tunis) phosphate, Florida Soft and Florida Waste Pond phosphate, Christmas Island phosphate, Makatea phosphate, Kosseir phosphate, Curacao (Caribbean Sea) phosphate specimens contain less than 2% fluorine.

It seems that the Curacao phosphate in the Dutch Island of Curacao off Venezuela contains the smallest amount of fluorine (0.38%). It also contains 1% Fe and Al oxides and its fluorine content is smaller than those of Florida, Tennessee and Western States. Small tonnages are imported into U. S. A. for stock feeds. The production is not much and in 1949 was 65000 tons.

The Makatea island about 120 miles north of Tahiti contains phosphate deposits having 1.2% F and 1% oxides of Fe and Al. The production in 1948 was 185000 tons. Christmas Island in the Indian Ocean contains phosphates with 1.30% F and 0.8% oxides of Fe and Al. Shipment in 1949 was 239000 tons. Australia and New Zealand are leasing these deposits.

Amongst the African phosphates, Kosseir (Egypt) phosphates, unlike Safaga (near Cairo, Egypt) phosphate which contains 3.2% F and 1.7% Fe and Al oxides, contains 1.3% F and 0.92% Fe and Al oxides. Kosseir contains 6.5%  $CO_2$  and Safaga 4.1%  $CO_2$  larger than other phosphate rocks. In 1948, Egypt produced 350000 tons. Djebel, in the boundary line between Algeria and Tunis, has a phosphate rock containing 1% F and 1.5% Fe and Al oxides. Production in Algeria was 713000 tons in 1947 and in Tunis in 1930 was 3226000 tons.

In 1939, the French North Africa produced 3831000 metric tons and U. S. A. 5760627 tons in 1948, but, the fluorine content in African phosphate is usually smaller than American phosphate rocks.

Florida Pebble is found to be phosphatised lime which is on the point of changing into secondary apatite. Secondary apatite was also found to have been formed in the case of Constantine phosphate and an appreciable quantity of carbonate was found between the granules which represented phosphatised fossil remains such as Nummulites, Oolites and sea shells. Examination of other North African phosphates showed that, like Constantine phosphate, they had all been built up from fossil remains of inhabitants of the sea.

North African phosphates are of a relatively soft, sandy character; they contain a very large proportion of fines as shipped and are easily ground to a high degree of fineness. They are the most successful of all phosphates for use as ground material for direct application as a fertilizer and, on the other hand, the output of certain mines, which produce a very hard material, is very highly esteemed for metallurgical purposes. Examples of the latter are the product of



one of the Kalaa Djerda (Tunisia) Company's mines and M'Zaita (Algeria). The Khouribga (Morocco) phosphate rock bed is relatively soft and requires a minimum of drilling and blasting.

The Egyptian deposits at Safaga and Kosseir are phosphorites in Cretaceous sediments and are similar to the Tunisian deposits. The grade of Egyptian phosphate ranges from 66-68% BPL. The rock is higher in carbonates than most phosphates.

In a previous paper, it has been stated as follows :—

“As the naturally occurring soft phosphate are abundant in Africa, North America, Oceania and other parts of the world and the natural deposits appear to be almost inexhaustible and the material is cheap, a greater utilization of the naturally occurring soft calcium phosphate, free from calcium fluoride, is desirable in growing crops, specially grass.”

It is evident from the foregoing pages that none of the natural phosphate deposits are completely free from fluorine. It seems that the Curacao phosphate has the smallest amount of fluorine (0.38%). Most other phosphates have larger amount of fluorine than this. Consequently, for direct addition of phosphate rocks mixed with organic matter, as emphasised in previous publications, the soft phosphate rocks containing small amounts of fluorine (less than 2%), such as those obtained from Curacao, Christmas Island, Makatea phosphate, Tunis phosphate, (Djebel M'Dilla), Kosseir phosphate, Florida Soft and Florida Waste Pond phosphate, are most suitable.

It is interesting to note that the Reno Phosphate Company of Paris deal with the North African Gafsa, phosphate, containing 2.35% fluorine and 0.72%  $\text{Fe}_2\text{O}_3$  and 0.52%  $\text{Al}_2\text{O}_3$  and their sale at present is nearly half a million tons per year, and, this is mostly used for direct addition without conversion into superphosphate.

There are phosphate rocks in Wyoming, Utah, Idaho and Montana containing 0.4 to 0.66% fluorine. But, like some of the Florida deposits, they are hard and may not be very suitable for direct addition to the soil. It is interesting that these deposits on the Western States of U. S. A. form approximately 60% of the phosphate reserves of U. S. A. estimated at 6431 million tons whilst the world reserve is 16867 million tons as recorded in the following table :—

WORLD RESERVES OF PHOSPHATE ROCK

Country				(Reserves metric tons)
United States	...	...	...	6,431,000,000
Tunisia	...	...	...	1,000,000,000
Algeria	...	...	...	1,452,000,000
Morocco	...	...	...	1,400,000,000
Egypt	...	...	...	179,000,000
Nauru & Ocean Islands	...	...	...	140,000,000
Makatea Islands	...	...	...	10,000,000
Angaur Island	...	...	...	3,000,000
Rosa Islands	...	...	...	3,000,000
Palestine	...	...	...	4,000,000
Total high grade				10,622,000,000

Country				(Reserves metric tons)
Russia	...	...	...	5,568,000,000
Spain (Murcia)	...	...	...	10,000,000
Siberia	...	...	...	667,000,000
Total low grade				6,245,000,000
Grand total				16,867,000,000

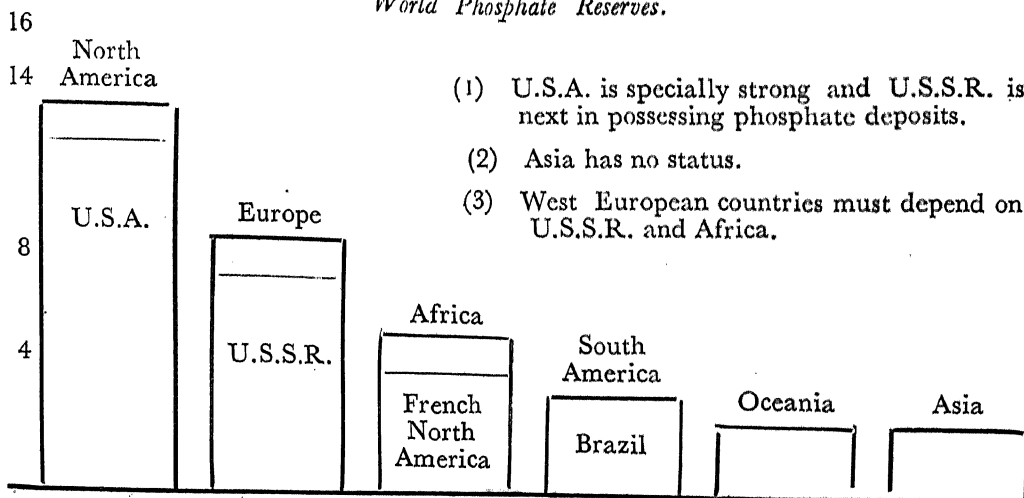
It is clear, therefore, that U. S. A. is specially strong in phosphate reserves. Next is U. S. S. R. But the Kola phosphate of this Union which is an extensive deposit is hard and is of the igneous type not suitable for direct addition but has to be converted into superphosphate. About 1930, on the Kola Peninsula not far from Murmansk, a huge igneous deposit of apatite was discovered in U. S. S. R. and since then this deposit has been developed into one of the largest sources of phosphate rock in the world. As the Murmansk port is open all the year round, most of the Kola deposit is shipped by ocean vessels in most countries of Europe for superphosphate manufacture. But apatite is a crystalline mineral and is not porous like the sedimentary phosphate deposits of North Africa or North America and reacts slowly with weak acids. When apatite grains are treated with sulphuric acid, they are attacked only on the surface whilst the sedimentary phosphates, being porous, absorb acid within their pores and react quickly. Apatite requires three times as long as sedimentary rocks for completion of the chemical change for the manufacture of superphosphate.

Apart from the Kola deposit, many deposits of sedimentary phosphate rocks are being mined in different parts of U. S. S. R. but their phosphate content is not high. Low grade sedimentary phosphates obtained from different parts of U. S. S. R. have been finely ground for direct application to the soil.

In the Kozak Republic in the Asiatic U. S. S. R. there are phosphate rock deposits, but, it seems that Asia, as a whole, has no status in natural phosphatic rock reserves. North-West Europe has to depend on North Africa and U. S. S. R. for purchasing phosphate rocks.

It is very interesting that a sample of Utah-Wyoming phosphate is so low in fluoride.

#### *World Phosphate Reserves.*



- (1) U.S.A. is specially strong and U.S.S.R. is next in possessing phosphate deposits.
- (2) Asia has no status.
- (3) West European countries must depend on U.S.S.R. and Africa.

## CALCIUM PHOSPHATES INCREASE NITROGEN FIXATION BY SUCROSE IN SWEDISH SOIL

In my Presidential Address to the National Academy of Sciences, India, in 1952 and in subsequent publications it was pointed out that the nitrogen fixation obtained by the slow oxidation of all types of organic substances when mixed with soil is intensified markedly when calcium phosphate or finely divided phosphate rocks or bone or basic slag is also present in the system. We have insisted that whenever organic matter either as green manure or straw or dung is ploughed in the soil, it should always be reinforced with calcium phosphate, because, this mixture fixes atmospheric nitrogen markedly and can supply nitrogen, potash and available phosphate to crops. The future of permanent agriculture all over the world depends on a proper utilisation of all types of organic matter photosynthesised by absorption of solar light mixed with naturally occurring phosphate rocks or basic slag obtained from the expanding steel industries of the world. In our recent experiments we have also utilised water hyacinth, which is well known to be rich in potash containing 2.35% nitrogen and 40% carbon analysed in the dry condition, as an energy material when mixed with basic slag in the fixation of atmospheric nitrogen. In these experiments we have not only used soils obtained in India but Swedish soil also has been used. The composition of the Swedish soil collected from a field in the Royal College of Agriculture, Uppsala-7 and the analysis of the North-African rock phosphate and Tata basic slag utilised are given below :—

### *Analysis of Swedish Soil*

Silica (HCl insoluble)	...	...	77.925%
Sesquioxide	...	...	12.26
Fe <sub>2</sub> O <sub>3</sub>	...	...	5.4000
CaO	..	...	1.19
MgO	...	...	3.1141
K <sub>2</sub> O	..	...	1.2012
P <sub>2</sub> O <sub>5</sub>	...	...	0.2250
Average P <sub>2</sub> O <sub>5</sub> (1% citric acid)	...	...	0.0830
Ex-Ca (N-NaCl)	...	...	10.4 m. e. per cent.
Total carbon	...	...	1.2072
Total nitrogen	...	...	0.1470

### *Analysis of North-African Rock Phosphate*

	Silica %	Fe <sub>2</sub> O <sub>3</sub> %	P <sub>2</sub> O <sub>5</sub> %	K <sub>2</sub> O %	CaO %	MgO %
A ...	1.68	0.00	19.6398	9.0212	10.6597	1.1588
B ...	4.32	0.00	26.3406	8.8424	13.2810	1.9193
C ...	5.00	0.00	24.1432	7.5584	7.4560	2.0822
D <sub>1</sub> ...	2.61	0.00	19.2381	1.1385	6.2327	1.6296
D <sub>2</sub> ...	2.52	0.00	25.2598	1.8489	6.2327	
Tata basic slag	23.66	38.90	7.5965	9.0736	34.3675	5.2870

(sesquioxide)

This soil was mixed with pure sucrose as energy material and the mixture was exposed to light and one set kept in the dark in presence or absence of different types of phosphates and the moisture content of the system was kept at 20%. Some of the results obtained at 25° are recorded below :—

Soil+1.5% carbon as Sucrose

	Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Increase in nitrogen %	Efficiency (nitrogen fixed in milligram per gram of carbon oxidised)
EXPOSED	0	2.3568	0.1470	...	...	...
	150	1.4833	0.1656	0.8735	0.0186	21.29
	300	1.2723	0.1682	1.0845	0.0262	28.41
COVERED	0	2.3568	0.1470	...	...	...
	150	1.7247	0.1554	0.6321	0.0084	13.28
	300	1.5036	0.1598	0.8532	0.0128	15.01

Soil+1.5% Carbon+Tricalcium Phosphate. (0.25%  $P_2O_5$ )

EXPOSED	0	2.3568	0.1470	...	...	...
	150	1.4112	0.1733	0.9456	0.0313	33.16
	300	0.9248	0.1958	1.4320	0.0488	34.13
COVERED	0	2.3568	0.1470	...	...	...
	150	1.6137	0.1605	0.7431	0.0135	18.51
	300	1.5432	0.1628	0.8136	0.0158	19.52

Soil+Sucrose+North-African Rock Phosphate A. (0.25%  $P_2O_5$ )

EXPOSED	0	2.3568	0.1470	...	...	...
	150	1.4132	0.1862	0.9436	0.0392	41.54
	300	1.1518	0.1992	1.2050	0.0522	43.36
COVERED	0	2.3568	0.1470	...	...	...
	150	1.6787	0.1608	0.6781	0.0138	20.31
	300	1.4612	0.1658	0.8956	0.0188	21.03

Soil+Sucrose+North-African Rock Phosphate B. (0.25%  $P_2O_5$ )

EXPOSED	0	2.3568	0.1470	...	...	...
	150	1.3725	0.1885	0.9843	0.0415	42.16
	300	1.1616	0.1952	1.1431	0.0482	42.38
COVERED	0	2.3568	0.1470	...	...	...
	150	1.6877	0.1618	0.6891	0.0148	21.50
	300	1.4433	0.1685	0.9135	0.0215	23.61

	Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Increase in nitrogen %	Efficiency (nitrogen fixed in milligram per gram of carbon oxidised)
Soil + Sucrose + North-African Rock Phosphate C. (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	2.3568	0.1470	...	...	...
	150	1.3622	0.1890	0.9946	0.0389	39.10
	300	1.1948	0.1932	1.1620	0.0462	39.81
COVERED	0	2.3568	0.1470	...	...	...
	150	1.6636	0.1597	0.6932	0.0127	18.41
	300	1.4315	0.1648	0.9253	0.0178	19.31
Soil + Sucrose + North-African Rock Phosphate D. (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	2.3568	0.1470	...	...	...
	150	1.3699	0.1863	0.9869	0.0393	39.81
	300	1.1414	0.1957	1.2154	0.0487	40.01
COVERED	0	2.3568	0.1470	...	...	...
	150	1.6832	0.1595	0.6736	0.0125	17.61
	300	1.4515	0.1629	0.9053	0.0159	18.51

The foregoing results show that when a Swedish clay soil containing 0.147% nitrogen mixed with sucrose is allowed to undergo slow oxidation in the air, there is marked nitrogen fixation which is more than double in light than in dark. When mixed with different calcium phosphates, the nitrogen fixation is considerably increased; and, that obtained in light is again more than double than that kept in the dark. In these experiments carried on at a temperature of 25° appreciable nitrogen fixation has been obtained after an interval of 5 months because of the compact nature of the clay soil, the aeration is inadequate and, hence, the velocity of oxidation of the sucrose is small. In Uppsala where the average temperature is about 5° in the fields the oxidation will be much slower, but it is expected that after 6 or 7 months, appreciable fixation will take place and the fertility is improved, specially in presence of phosphates. This is the reason why Professor G. Torstensson of the Royal College of Agriculture (Uppsala) obtained an increase of 15—20% in the yield of oats and barley in his field experiments by ploughing in straw.

Our experiments on nitrogen fixation have been corroborated by Dr. H. W. Kerr at Brisbane, by Prof. Shri Ranjan and Mr. Bhattacharya of the Botany Department, Allahabad University, by B. Ramamoorthy of the Indian Institute of Agricultural Research, New Delhi, and by Mr. Sulaiman of the Dacca University, Dacca. It is stated that results obtained in Hawaii (Handbook of Hawaiian soils, p. 190; also International Sugar Journal 1937, 39 : 419, 420), inexplicable under

the biological hypothesis, can be explained by the photochemical hypothesis of Dhar and co-workers. Moreover Sir John Russell (Nature, April 11, 1936, p. 629) has stated as follows : "Professor Dhar leads the school of thought which believes that nitrification in soils and nitrogen fixation from the atmosphere are especially in the tropics photochemical, at least as much as bacterial action. Prof. Dhar has produced an indisputable evidence of increase in available soil nitrogen and crop yields following the application of molasses. Prof. Dhar suggests that a most valuable use can be made of molasses in reclaiming alkaline land. There are 4 million acres of infertile alkaline land in India and irrigation practices are increasing the area. The economic reclamation of these lands is one of country's greatest agricultural problems the solution of which Prof. Dhar's work is pointing the way."

In the present investigations of G. Bjälfve on the decomposition of straw and other organic substances, he has found an increase in the total nitrogen content of the system more in light than in the dark when sand is mixed with straw or starch.

Mr. J. I. Rodale of Pennsylvania, Editor of "Organic Farming" in "The Farmer" (1949 winter issue, page 10) has stated as follows : "To say that this is an exciting situation is to put it mildly. But if Dr. Dhar is right and he seems to have done the experimental work to prove it, we seem to be on the threshold of something spectacular. In the case of making compost by the aeration method, some of the nitrogen is lost. At any rate, the total nitrogen content of compost is not very high about one to two per cent. By placing our organic matter in a thin layer in the field and discing it in the upper four inches, there is a much slower oxidation than in the composting process, and in the field, more nitrogen is fixed."

Dr. Charlotte M. Hoak of California has put the position as follows in Proc. National Inst. Sci. India 10 (1953) : "It is with interest that I have read and digested the helpful chemical research in agricultural fields done by your leader Dr. N. R. Dhar. The various reprints of the Proceedings of the National Academy of Sciences, India and his invaluable book on Biochemistry should be in the hands of every progressive agriculturist; of special interest to us in the semi-arid Southwest is the reclamation of Usar (alkaline) land by treatment of Molasses and Press mud. Of great interest throughout the country is the new light thrown on the direct nitrification of the soil."

The Editor of "Farmer", Mr. Newman Turner, has recorded as follows :—

".....But Dr. Dhar's findings are thoroughly sound. We have practised them for nearly 7 years at Goosegreen Farm with great success."

#### PHOSPHATE ROCK AND TATA BASIC SLAG IMPROVE NITROGEN FIXATION IN INDIAN SOILS MIXED WITH COWDUNG, SUCROSE Etc.

Moreover, we have carried on a large number of experiments with an ordinary soil collected from a land in front of the Sheila Dhar Institute of Soil Science, University of Allahabad. Dung and sucrose have been used as energy materials in these experiments and different calcium phosphates and basic slag have been used

to increase the nitrogen fixation. In the following tables the analyses of the materials used are recorded :—

*Analysis of Inferior Soil*

		%	pH (1 part Soil + 2.5 water) 8.9
Moisture	...	2.47	
Loss on Ignition	...	3.68	
SiO <sub>2</sub>	...	74.54	
Sesquioxide	...	12.47	
Fe <sub>2</sub> O <sub>3</sub>	...	4.48	
CaO	...	2.93	
MgO	...	1.83	
K <sub>2</sub> O	...	0.287	
P <sub>2</sub> O <sub>5</sub>	...	0.192	
Carbon	...	0.239	
Nitrogen (Salicylic Acid method)		0.0436	
Available P <sub>2</sub> O <sub>5</sub>	...	0.0273	
Ex-Calcium	..	5.53 m.e. per cent.	
Azotobacter count	...	1.2 million/per gram.	
Fungus count	...	25000/per gram.	

*Analysis of Dung*

		%
Moisture	...	4.90
Loss on Ignition	...	63.46
Ash	...	36.53
Silica	...	30.66
CaO	...	2.52
MgO	...	0.9342
K <sub>2</sub> O	...	0.7216
P <sub>2</sub> O <sub>5</sub>	...	0.6729
Total carbon	...	28.63
Total nitrogen	...	1.0108

*Analysis of Sucrose*

Total carbon	...	41.20 per cent.
„ nitrogen	...	0.00

*Analysis of Trichinopoly Rock Phosphate*

Silica	...	...	6.3	Per cent
Fe <sub>2</sub> O <sub>3</sub>	...	...	4.2	
Al <sub>2</sub> O <sub>3</sub>	...	...	26.9	
Sesquioxide	...	...	31.1	
P <sub>2</sub> O <sub>5</sub>	...	...	27.8	
CaO	...	...	20.8	
MgO	...	...	1.92	
Available P <sub>2</sub> O <sub>5</sub>	...	...	1.0	
(1% Citric acid)	...	...		

*Analysis of Tata Basic Slag*

Total P <sub>2</sub> O <sub>5</sub>	...	...	7.5965
Available P <sub>2</sub> O <sub>5</sub>	...	...	4.46
Silica	...	...	23.66
P <sub>2</sub> O <sub>5</sub>	...	...	7.5965
K <sub>2</sub> O	...	...	9.0736
CaO	...	...	34.3675
MgO	...	...	5.2870

*Analysis of Bihar Rock Phosphate*

			%
SiO <sub>2</sub>	...	...	5.52
Fe <sub>2</sub> O <sub>3</sub>	...	...	3.92
Al <sub>2</sub> O <sub>3</sub>	...	...	23.12
P <sub>2</sub> O <sub>5</sub>	...	...	27.9
CaO	...	...	11.8
MgO	...	...	0.30

The results regarding the fixation of atmospheric nitrogen using sucrose or dung as energy material are recorded below :

Soil + Sucrose.

	Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Change in total nitrogen %	Efficiency (amount of nitrogen fixed in mg per gram of carbon oxidized)
EXPOSED	0	1.7303	0.0420	...	...	...
	60	1.2588	0.0573	0.4715	0.0153	32.57
	120	1.2171	0.0613	0.5132	0.0193	37.59
	180	1.1155	0.0675	0.6118	0.0255	41.49
COVERED	0	1.7303	0.0420	...	...	...
	60	1.4853	0.0461	0.2450	0.0041	16.88
	120	1.4291	0.0489	0.3012	0.0069	23.12
	180	1.3195	0.0521	0.4108	0.0101	24.82



	Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Change in total nitrogen %	Efficiency (amount of nitrogen fixed in mg per gram of carbon oxidized)
Soil + Sucrose + Tata Basic Slag. (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.7151	0.0392	...	...	...
	60	1.0217	0.0750	0.6934	0.0358	51.67
	120	0.8695	0.0378	0.8456	0.0486	57.51
	180	0.7287	0.0960	0.9864	0.0568	57.58
COVERED	0	1.7151	0.0392	...	...	...
	60	1.3295	0.0497	0.3856	0.0105	27.84
	120	1.2633	0.0520	0.4518	0.0128	28.51
	180	1.2020	0.0546	0.5131	0.0154	30.01
Soil + Sucrose + Trichinopoly Rock Phosphate (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.7258	0.0412	...	...	...
	60	1.1822	0.0776	0.5436	0.0364	67.14
	120	0.9819	0.0918	0.7439	0.0506	68.01
	180	0.9687	0.0949	0.7561	0.0537	71.02
COVERED	0	1.7258	0.0412	...	...	...
	60	1.3650	0.0525	0.3608	0.0113	31.31
	120	1.3231	0.0551	0.4027	0.0139	34.51
	180	1.2172	0.0588	0.5086	0.0176	34.60
Soil + Sucrose + Bihar Rock Phosphate (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.7258	0.0412	...	...	...
	60	1.1367	0.0788	0.5891	0.0376	63.82
	120	1.0207	0.0900	0.7051	0.0488	69.21
	180	0.9820	0.0938	0.7438	0.0526	70.71
COVERED	0	1.7258	0.0412	...	...	...
	60	1.3626	0.0519	0.3632	0.0107	29.51
	120	1.3253	0.0545	0.4005	0.0133	33.20
	180	1.2138	0.0582	0.5120	0.0170	33.21
Soil + Sucrose + Tricalcium Phosphate (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.7288	0.0417	...	...	...
	60	1.1674	0.0790	0.5614	0.0373	66.44
	120	1.0435	0.0836	0.6853	0.0491	71.64
	180	0.9962	0.0955	0.7326	0.0538	73.43
COVERED	0	1.7288	0.0417	...	...	...
	60	1.3487	0.0537	0.3801	0.0120	31.57
	120	1.2860	0.0564	0.4428	0.0147	33.19
	180	1.2354	0.0598	0.4934	0.0181	36.66

	Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Change in total nitrogen %	Efficiency (amount of nitrogen fixed in mg per gram of carbon oxidized)
Soil + DUNG						
EXPOSED	0	1.7262	0.0942	...	...	...
	60	1.5077	0.0990	0.2185	0.0048	22.42
	120	1.3411	0.1044	0.3851	0.0102	26.51
	180	1.2120	0.1083	0.5142	0.0141	27.55
COVERED	0	1.7262	0.0942	...	...	...
	60	1.5230	0.0970	0.2032	0.0023	13.86
	120	1.4248	0.0988	0.3014	0.0046	15.33
	180	1.2647	0.1015	0.4615	0.0073	15.98
Soil + DUNG + Tata Basic Slag (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.7125	0.0925	...	...	...
	60	1.0373	0.1208	0.6752	0.0293	41.93
	120	0.9489	0.1246	0.7641	0.0321	42.03
	180	0.9232	0.1279	0.7893	0.0354	44.81
COVERED	0	1.7125	0.0925	...	...	...
	60	1.3713	0.0984	0.3412	0.0059	17.50
	120	1.2974	0.1010	0.4151	0.0085	20.34
	180	1.2277	0.1030	0.4848	0.0105	21.76
Soil + DUNG + Trichinopoly Rock Phosphate (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.6722	0.0934	...	...	...
	60	1.1704	0.1182	0.5018	0.0248	49.46
	120	0.9899	0.1285	0.6823	0.0351	51.39
	180	0.9512	0.1328	0.7210	0.0394	54.60
COVERED	0	1.6722	0.0934	...	...	...
	60	1.3407	0.1005	0.3315	0.0071	21.43
	120	1.2911	0.1020	0.3811	0.0086	22.51
	180	1.2030	0.1046	0.4692	0.0113	24.00
Soil + DUNG + Bihar Rock Phosphate (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.6722	0.0934	...	...	...
	60	1.1020	0.1236	0.5702	0.0302	53.01
	120	0.9890	0.1311	0.6832	0.0377	55.22
	180	0.8266	0.1407	0.8456	0.0473	55.89
COVERED	0	1.6722	0.0934	...	...	...
	60	1.3312	0.1003	0.3410	0.0069	20.38
	120	1.2599	0.1023	0.4123	0.0089	21.77
	180	1.1908	0.1054	0.4814	0.0120	24.96

	Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Change in total nitrogen %	Efficiency (amount of nitrogen fixed in mg per gram of carbon oxidized)
Soil + DUNG + Tricalcium Phosphate (0.25% P <sub>2</sub> O <sub>5</sub> )						
EXPOSED	0	1.7234	0.0936	...	...	...
	60	1.1092	0.1279	0.6142	0.0343	55.89
	120	1.0288	0.1327	0.6946	0.0391	56.30
	180	1.0183	0.1359	0.7051	0.0420	59.58
COVERED	0	1.7234	0.0936	...	...	...
	60	1.3524	0.1031	0.3610	0.0095	26.18
	120	1.3019	0.1048	0.4215	0.0112	26.73
	180	1.2721	0.1063	0.4513	0.0127	28.12

It is evident from the foregoing results that when a heavy dose of sucrose is mixed with this ordinary soil, there is considerable nitrogen fixation even in the absence of phosphates. The original nitrogen content of the soil is 0.043%, but, due to the fixation of nitrogen in the slow oxidation of sucrose, the nitrogen content of the system goes up to 0.0675%, i.e., an increase of more than 50% of the total nitrogen in light. In the dark, the nitrogen increase is less and the total nitrogen goes up to 0.052%. As soon as phosphates are added, the nitrogen content shows an increase of 250% in light whilst in the dark, the nitrogen increase is about 40% to 45% in presence of phosphates. These remarkable results conclusively prove that organic matter mixed with phosphates forms a very valuable source of land fertility improvement.

With dung, when a heavy dose is added, the mixture of soil and dung, at the beginning, shows a nitrogen content of 0.0942%. In absence of phosphates and in presence of light, the nitrogen content goes up to 0.108%, i.e., an increase of about 15%. In presence of Bihar Rock phosphate the total nitrogen content of the mixture in light goes up to 0.1407% from 0.0934%, showing an increase of about 50%.

Some of our recent observations on the influence of different phosphates on nitrogen fixation by *Melia Azadiractta* are recorded in the following tables :—

200 gm. soil + 0.5% carbon as Neem (*Melia Azadiractta*) leaf.

Temperature—37°

Period of exposure in days	Total organic carbon	Total nitrogen	Azotobacter in millions per gram	Efficiency (Mgs. of N <sub>2</sub> fixed per gm. of carbon oxidised.)
Exposed to light of a 500 Watt electric bulb				
0	0.912	0.0561	1.8	...
90	0.768	0.0599	...	26.3
180	0.706	0.0613	4.3	25.2
Kept in the dark				
0	0.912	0.0561	1.8	...
90	0.813	0.0575	...	14.1
180	0.770	0.0581	6.8	14.1

200 gms soil + 0.5% carbon as Neem leaf + 0.2%  $P_2O_5$  as  $CaHPO_4$

Exposed to light				
0	0.912	0.0559	1.8	...
90	0.748	0.0630	...	43.2
180	0.691	0.0651	7.1	41.6
Kept in the dark				
0	0.912	0.0559	1.8	...
90	0.791	0.0587	...	23.1
180	0.756	0.0593	10.8	21.8

In presence of potassium chloride the efficiency increases.

Similar results were obtained with other phosphates and the results are summarised in the following table :—

Efficiency after 90 days		
	Light	Dark
No phosphate	26.3	14.1
0.25% $P_2O_5$ as $Ca(H_2PO_4)_2$	39.3	18.9
0.25% $P_2O_5$ as $CaHPO_4$	43.2	23.1
0.25% $P_2O_5$ as $Ca_3(PO_4)_2$	40.8	21.2
0.25% $P_2O_5$ as $FePO_4$	32.5	18.1
0.25% $P_2O_5$ as $AlPO_4$	33.0	17.8

The phosphates of calcium increase nitrogen fixation more markedly than those of iron and aluminium.

Recently, Dhar and co-workers have obtained marked nitrogen fixation when the whole of the leguminous plants like sunhemp (*Crotalaria Juncea*) or lucerne or clover is ploughed in the soil and allowed to undergo slow oxidation and, this nitrogen fixation is greatly enhanced by adding calcium phosphate and by light absorption. Some of our results are recorded here :—

200 gms. soil + 0.5% carbon as lucerne (*Medicago Sativa*)

Temperature—26°				
Period of exposure	Total organic carbon	Total nitrogen	Azotobacter in millions per gram soil	Efficiency
Exposed to light				
0	0.901	0.0643	2.0	...
90	0.724	0.0718	...	42.3
180	0.658	0.0743	4.5	41.2
Kept in the dark				
0	0.901	0.0644	2.0	21.7
90	0.768	0.0673	...	...
180	0.712	0.0682	7.6	20.1

200 gms. soil + 0.5% carbon as lucerne + 0.25%  $P_2O_5$  as  $CaHPO_4$

Period of exposure	Total organic carbon	Total nitrogen	Azotobacter in millions per gram soil	Efficiency
Exposed to light				
0	0.902	0.0644	2.0	..
90	0.703	0.0781	...	68.8
180	0.640	0.0820	8.1	67.1
Kept in the dark				
0	0.903	0.0646	2.0	---
90	0.732	0.0706	...	35.0
180	0.690	0.0718	11.2	33.7

Similar results were obtained with other phosphates and the results are summarised below

			Efficiency after 90 days	
			Light	Dark
No phosphate		...	42.3	21.7
0.25% $P_2O_5$ as $Ca(H_2PO_4)_2$		...	55.1	28.4
" " as $CaHPO_4$		...	68.8	35.0
" " as $Ca_3(PO_4)_2$		...	61.0	31.4
" " as $FePO_4$		...	45.4	25.2
" " as $AlPO_4$		...	44.8	23.6

In these experiments the total nitrogen was determined by the salicylic acid—thiosulphate reduction Kjeldahl method and the organic carbon according to iodometric method of W. Robinson, McLean and Williams.

Chemical composition of the soil used is as follows :—

CaO—1.002% ; MgO—1.59% ;  $P_2O_5$ —0.084% ;  $K_2O$ —0.989% ; total organic carbon—0.414% ; total nitrogen—0.0435% and pH—7.6.

Analysis of Neem ( <i>Melia Azadiractta</i> ) leaf		Analysis of lucerne
Ash	... 10.9 %	10.45 %
Silica	... 4.35%	---
Sesquioxide	... 2.52%	0.3 %
CaO	... 1.65%	1.68 %
MgO	... 0.52%	...
$K_2O$	... 1.24%	3.42 %
$P_2O_5$	... 0.138%	0.721%
C	... 25.42 %	42.1 %
N	... 0.674%	2.09 %

In the following tables the results obtained in the fixation of nitrogen by the oxidation of the carbonaceous substances present in the soil humus have been recorded. This soil was good and contained 4.06% CaO, 0.418%  $P_2O_5$  and 0.2472% total nitrogen and to this no organic matter was added but still an appreciable nitrogen fixation is observed and it increases by adding calcium phosphate and potassium chloride :—

200 gms. of soil exposed to air			Temperature—25°
Period of exposure in days	Total organic carbon	Total nitrogen	Efficiency
Exposed to light			
0	1.4556	0.2472	—
90	1.3500	0.2515	40.7
Kept in the dark			
0	1.4556	0.2472	—
90	1.4010	0.2476	25.6
200 gms. soil + 0.05% $P_2O_5$ as $Ca_3(PO_4)_2$ + 1% KCl			
Exposed to light			
0	1.4556	0.2472	—
90	1.2840	0.2595	71.6
Kept in the dark			
0	1.4556	0.2472	—
90	1.3710	0.2505	39.0

Russell has reported that 41000 K Cal are liberated from each acre of land at Rothamsted per day manured by 14 tons of farm yard manure containing 200 lbs. of nitrogen per acre. In other words per year the liberation of Kilo calories is  $41000 \times 365$ . It is well known that 1 Kilo of carbohydrate when oxidized produces 4100 Kilo calories. Hence the amount of carbohydrate oxidized per year from the Rothamsted land per acre amounts to 3650 Kgs. In other words the amount of carbon oxidized is  $\frac{2}{3} \times 3650$  i.e. 1460 Kgs. per acre per year.

It is well known that the carbon/nitrogen ratio of farm yard manure is approximately 20:1. Hence the amount of carbon introduced in these experiments at Rothamsted is 4000 lbs per acre which is equivalent to 1812 Kgs. Hence the percentage of carbon oxidized per year from the farm yard manure carbon is 80.6.

In our experiments we have obtained a nitrogen fixation approximately 25 milligrams per gram of carbon oxidized with dung. Hence in the oxidation of 1460 Kgs of carbon the amount of nitrogen fixed per acre is 18.25 Kgs. i.e. of the order of 35 lbs per acre.

Bear has reported that on adding 5 tons of artificial fertilizer per acre over a period of 15 years, the fertilized soil contained 60800 lbs of organic matter, whereas the unfertilized land contain 42800 lbs. in 2 million lbs of soil. This represents an increase of 9 tons of organic matter per acre i.e. an increase of 40% in 15 years.

To another plot 190 tons of manures were applied, the organic matter of this field was 73600 lbs. By comparing the crop increase in this manured plot with that on the unfertilized plot one might have expected the organic matter content of soil to be 64100 lbs., but the observed amount is higher by 73600—64100 lbs. =9500 lbs. If we assume that the manure contained 25% dry matter 190 tons supplied 95000 lbs. organic matter, of this only 10% remained in the soil at the end of 15 years.

The carbon supplied in the experiment of Bear with dung is roughly  $\frac{2}{3}$  of the solid organic matter i.e. 38000 lbs. and the nitrogen is  $\frac{1}{20}$  of this amount i.e. 1900 lbs.

The organic matter content of the soil to which artificial fertilizers have been added was 60800 lbs. the carbon content of which is  $\frac{2}{3}$  i.e. 24320 lbs. and nitrogen is  $\frac{1}{10}$  i.e. 2432 lbs.

In the dunged plot the organic matter was 73600 lbs. the carbon content of which is  $\frac{2}{3}$  i.e. 29440 lbs. and nitrogen is 2944 lbs.

The difference between the dunged and artificial fertilizer plots as regards carbon and nitrogen is 5120 and 512 lbs. respectively.

Hence the nitrogen increase in the dunged over the artificial fertilizer plot per year is  $\frac{512}{15} = 34.1$  lbs. In Bear's experiment 190 tons of dung were added in 15 years i.e. at the rate of 12.6 tons per year.

It appears that the nitrogen fixation in the Rothamsted and the experiments of Bear in U. S. A. was of the same order.

Bear has calculated that 9500 lbs. of organic matter is contributed by the dung i.e., carbon is 3800 lbs. and nitrogen is 380 lbs. Hence the addition of nitrogen per year in lbs. is  $\frac{380}{15} = 25.3$  lbs. Even if we assume that this nitrogen is obtained from the nitrogenous matter introduced in the dung and this assumption seems incorrect, the increase of nitrogen per year in the dunged plot over the plot fertilized by artificials is actually about 10 lbs. higher than that assumed by Bear.

## PHOSPHATES STABILISE PROTEINS IN SOILS

It seems that phosphates play a vital role in the improvement and maintenance of the nitrogen status of soils. The proteins that are present in the soil humus are likely to be stabilised by the formation of the nucleo-proteins, phospho-proteins etc. with the combination of proteins and phosphates or other substances. In this connection the following lines from Russell's "Soil Conditions & Plant Growth," 1950, are of interest: "It is not known in what form the phytin and nucleic acids occur in the organic matter, though presumably, most of the nucleic acid must be in nucleo-proteins nor in which humic fraction they are concentrated. They must be protected in some way from the soil enzymes as they are readily dephosphorylated if mixed with the soil, i. e. they have their phosphate groups

split off as inorganic ortho-phosphate anions. This is also shown independently by the fact that these organic phosphates can only be extracted in good yield from the humic material if it is subjected to fairly drastic pre-treatment."

Moreover, the organic matter present in the soil or added to it undergoes slow oxidation in the soil aided by sunlight and presence of alkali and fixes nitrogen of the air and forms proteins in this process. Under ordinary conditions the proteins formed undergo ammonification and nitrification.

Hence, along with nitrogen fixation and formation of proteins due to the oxidation of energy materials, ammonification and nitrification which oppose the increase of proteins in the soil, take place and, thus, the amount of protein remaining in the soil tends to decrease. Hence, the apparent efficiency of nitrogen fixation, i. e. the amount of nitrogen fixed per gram of carbon of the organic matter oxidised, appears to fall off when ammonification and nitrification take place. But in presence of large amounts of phosphates in the system, more or less stable phosphoproteins are formed by the combination of proteins and phosphorus compounds. These compounds seem to resist nitrification and ammonification and loss of nitrogen better than proteins alone. This appears to be an important reason why the efficiency of nitrogen fixation in soils, both under sterile and unsterile conditions, appears larger in presence of increasing quantities of phosphates.

### MECHANISM OF NITROGEN FIXATION

In explaining photo-synthesis in plants, Dhar postulated in 1933 that the important photo-chemical reaction is the decomposition of water by absorption of light according to the following equation :—



The hydrogen atom thus formed reduces the carbonic acid adsorbed on the leaves forming formaldehyde. In recent years this view of the mechanism of photosynthesis has been supported by the use of carbonic acid containing isotopic carbon. In explaining nitrogen fixation the best mechanism seems to be the same, i.e. the decomposition of water into H and OH by absorption of energy obtained from the oxidation of carbohydrates, celluloses, lignin, fats, coals etc. Moreover, in presence of light, the light energy, whether from the sun or artificial source, is absorbed by the system and utilised in increasing nitrogen fixation. In symbiotic nitrogen fixation also the same mechanism may be applicable.

For fixing 14 grams of nitrogen and forming ammonia by the interaction of molecular nitrogen and atomic hydrogen obtained by the decomposition of water as stated above, 336 K.Cal are needed. Hence, from the oxidation of a gram mol of glucose according to the equation  $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 = 6\text{CO}_2 + 6\text{H}_2\text{O} + 676 \text{ K. Cal}$ ,  
 $\frac{14 \times 676}{336}$  grs. of nitrogen can be fixed under ideal conditions. In other words, 0.39 gram of nitrogen should be fixed per gram of carbon oxidised. In many of our experiments in soils, fairly rich in calcium and phosphate, a nitrogen fixation of 100 mgms. with sugar candy and about 150 mgrs. with wheat straw has been observed per gram of carbon oxidised. Hence the efficiency of this type of nitrogen fixation in soils is  $150/390 \times 100 = 38\%$  with straw in light, and with sugar candy  $100/390 \times 100 = 25\%$ . In sterile conditions the efficiency in light is 21% with wheat straw; in the dark this efficiency is 10%. Hence the efficiency can be three times greater than the industrial methods of fixing nitrogen.



It is well known that in absence of moisture nitrogen fixation in soils does not take place, because water plays a prominent part as postulated in the mechanism of nitrogen fixation proposed above. The ammonia can readily be oxidised to nitrates in soils or nodules. Dhar and Mukherji (J. Indian Chem. Soc., 1934, 11, 727) have obtained amino acids readily by the action of nitrates on carbohydrates in presence of light using titania as photocatalyst. In symbiotic nitrogen fixation the energy required is supplied by the oxidation of the carbohydrates photosynthesised by the host plant and nitrogen fixation takes place chiefly in the nodules. In this process the possibility of the loss of nitrogen by the formation and decomposition of ammonium nitrite appears to be less than in our experiments where the facility for the oxidation of proteins, amino acids, ammonium salts obtained by fixation, is greater than in nodules. This is certainly one of the reasons why symbiotic nitrogen fixation frequently appears to be more efficient than nonsymbiotic fixation.

Ammonia is readily detected in nitrogen fixation by *Azotobacter* or *Clostridia* in culture media. In our experiments on nitrogen fixation in sand or soil with soluble carbohydrates or glycerol as energy material, there is marked increase of ammoniacal nitrogen in a short time.

### EFFICIENCY OF SYMBIOTIC NITROGEN FIXATION

P. W. Wilson (Biochemistry of Nitrogen Fixation, Madison, 1940) has reported that in nitrogen fixation by red clover using sucrose in sand culture, a nitrogen fixation of 1 gram has been obtained per 25 grams of dry plant material. Assuming that 40% of this plant material is carbon, the symbiotic nitrogen fixation by red clover becomes 100 mgms. per gram of carbon oxidised in symbiosis. It is very interesting, therefore, that the efficiency of symbiotic nitrogen fixation, which has always been considered to be about 10 times greater than that of non-symbiotic fixation, may be even smaller than the efficiency obtained in light in our experiments. In the manuring of fields with legumes, Weir has stated that under normal conditions 1 cwt., i.e. 112 lbs. of nitrogen, are added per acre, but usually the amount may be as small as 40—60 lbs. On the other hand, when 5—10 tons of leaves or straw are added to the soil, rich in calcium phosphate specially in tropical countries, the nitrogen addition may be much greater than with legumes. Moreover, legumes cannot be grown year after year in the same soil. Also, legumes make the soil certainly more acidic than straw or plant leaf and are known to be an acidic manure.

It is estimated that in the whole world, not more than 5 million tons of nitrogen of the air are fixed in the cultivated lands by legumes. Hence, the contribution of legumes in nitrogen supply is within 5 million tons, i.e., an amount almost identical to that produced in the nitrogen chemical industries.

It is well known that the presence of ammonium ions or nitrate ions in a system depresses the nitrogen fixation by *Azotobacter* in culture media, ammonium ion depressing it more than nitrate ion. Moreover, it has been stated that nitrogenous fertilizers often increase the growth of legumes, but, reduce considerably the amount of nitrogen fixed. It is well known that prairie soils are usually rich in ammonium salts and nitrates and that is why A. G. Norman has reported a fixation of 20 to 25 lbs. of nitrogen by soy beans growing in Iowan prairie soils. This fixation is much less than those observed in soils poor in nitrogen. It is believed that the *Rhizobia* in legumes can fix nitrogen more efficiently than *Azotobacter* or *Clostridia*. It has been stated that the respiration rate of *Azotobacter* and *Rhizobia* is high. It seems

that the haemoglobin in *Rhizobia* may cause the rapid oxidation of carbohydrates as in animals. Jensen has reported that in presence of molybdenum, lucerne, under favourable conditions can fix 100 mgms. of nitrogen daily per gm. of dry matter in the nodule which corresponds to 1.36 times its own nitrogen content. On the other hand, in our experiments on nitrogen fixation in light with sugar and soil containing 0.04% total nitrogen, the total nitrogen content went up to 250% higher than the nitrogen originally present in the soil when calcium phosphates were added to the system.

A. T. Virtanen has stated that molecular hydrogen is formed from sugars containing a heavy suspension of nodule bacteria. It is interesting to record that in the hydrogenation of nitrogen in the Haber-Bosch method of formation of ammonia, molybdenum has been found to be a good catalyst. Virtanen has stated that the protein synthesised in legumes undergoes hydrolysis into amino acids which can, under favourable conditions, pass into the soil or sand; but, Jensen did not observe a similar behaviour with *Azotobacter* growing on glucose containing Australian wheat soils. Virtanen, working at Helsinki, reported that upto 70% of the nitrogen fixed by peas and red clover, may be excreted in the soil in the form of aspartic acid or L-alanine. Thornton and Nicol, also, working at Rothamsted, reported that nitrogen excretion takes place when a legume, like lucerne, and a non-legume, like Italian rye grass, grow in sand. It seems that nitrogen excretion by legume is a sign of nitrogen fixation occurring at a greater speed than the nitrogen utilisation, and, this phenomenon seems to be retarded by the presence of carbohydrates just as nitrogen loss in the process of nitrification is retarded by carbohydrates.

Shutt, in Canada, found a net gain of 50 lbs. of nitrogen per acre by clover on light sandy soil. Lipman and Blair obtained an average annual gain of 54 lbs. of nitrogen per acre in cylinder experiments by growing legumes in rotation with maize, potatoes, oats and rye. On a sandy soil with inoculated soybeans, Fred obtained a gain of 65 lbs. of nitrogen per acre.

From the foregoing lines it is clear that in temperate countries approximately 50 lbs. of nitrogen are added by growing ordinary legumes. On the other hand, high fixations upto 400 to 500 lbs. have also been reported by L. Yankovitch in Tunis. The large fixation, i.e. 400 to 500 lbs. of nitrogen per acre, by peas, beans, vetches and lentils in Tunis, reported by L. Yankovitch (*Ann. Serv. Bot. Agron. Tunisie*, 1940, 16, 303), has to be ascribed to the poverty of total and available nitrogen in Tunisian soils. The generally accepted view is that soils poor in available nitrogen produce large fixations. It is necessary to examine the position very carefully. The legumes, like other plants, require lime, potash, phosphate and nitrates or ammonium salts for their growth. Hence, it is clear that along with lime, potash, and phosphate some amount of nitrate should be present for beginning of the growth of the host plant. It has also been stated that in soils containing fair amounts of nitrates the host plant roots are not easily affected by *Rhizobia*. Hence, under such circumstances, the nitrogen fixation is not likely to be developed. It is clear, therefore, that for the successful invasion of the host plant by *Rhizobia*, the available nitrogen status of the soil supporting the legume should be low. On the other hand, for a vigorous growth of the host plant, minerals are needed and the soil should be well supplied with minerals. Due to the presence of small amounts of ammonium salts or nitrate in the soil, the host plant will take root in the soil and will be infected by the *Rhizobia*. Once the *Rhizobia* enters the plant system, the nitrogen need of the host plant and bacteria can be met by the fixed nitrogen, because, the plant-*Rhizobia* system is a highly oxidising combination. The carbohydrates

photosynthesised by the plant are quickly oxidised leading to the formation of protein by nitrogen fixation. As soon as the proteins are produced in the system which is capable of undergoing oxidation, ammonium salts and nitrates may also be produced in the system from the protein oxidation and in this process ammonium nitrite is likely to be formed and it readily undergoes decomposition. Thus, the efficiency of nitrogen fixation will be lowered. Moreover, the aminoacids produced in the fixation may pass out of the system into the outside soil where formation of ammonia is easy and consequent loss is probable. Moreover, by the passage of these aminoacids to the soils, their fertility regarding nitrogen will increase and a part of the available nitrogen present in the soil may be absorbed by the plant roots and will be utilised by both the plant and the bacteria. The net result will be the decrease of the nitrogen fixing properties. In Rothamsted it has been stated that the available nitrogen is about 1 to 2% of the total nitrogen making 20 to 40 lbs. of available nitrogen per acre. It seems that these soils low in available nitrogen is better fitted for enhanced nitrogen fixation than soils which are sandy and the conditions are favourable for rapid oxidation. In our soils, the available nitrogen is about 100 lbs. per acre and as the temperature of our soils is high in plains, oxidation of the secreted protein or aminoacid will be abundant causing a marked loss of nitrogen and, hence, the final efficiency of the nitrogen fixation may not appear to be high. The average nitrogen fixation in Canada is reported to be 50 lbs. by Shutt per acre on a light sandy soil. Similar amount has been reported by Lipman and Blair. This low value is possibly due to the ease of the oxidation of the aminoacids and proteins present in the soil or passed into it from the synthesised proteins present in the host plant. It is clear, therefore, that the high nitrogen fixation reported in Tunis is due to the fact that the amount of available nitrogen present in the Tunis soils is low. In sandy soils, however, where oxidation conditions are very favourable, high nitrogen fixations are not expected. High nitrogen fixation should be associated with low available nitrogen and high phosphate content in the system, enough minerals and a proper pH, copious photosynthesis in the leaves of the host plant and marked oxidation capacity of the system in the earlier part of the symbiosis. If the ease of the oxidation in the symbiotic system continues, a large amount of the protein synthesised is likely to undergo oxidation with consequent loss of nitrogen in the gaseous state due to the formation and decomposition of the unstable substance, ammonium nitrite. Moreover, if the major portion of the proteins produced in the symbiosis passes out into the soil, a large proportion is likely to be lost as nitrogen gas. It seems that in countries like Finland, the efficiency of the process may be high in the beginning, but, later on, due to the secretion of the nitrogenous compounds and the subsequent loss, the efficiency of the process will fall. Hence, so far, people have got erratic results on symbiotic nitrogen fixation. The foregoing considerations are likely to throw light in explaining such results.

#### LARGE AMOUNTS OF NITROGEN ARE FIXED ON THE SOIL SURFACE BY THE CATALYTIC, PHOTOCHEMICAL AND BACTERIAL OXIDATION OF ORGANIC MATTER PRODUCED BY PHOTOSYNTHESIS

It is estimated that 35 billion kilograms, i.e., 34,750 million tons of carbon are added every year to the earth. From our experiments, we find that 40% of the carbon is oxidised in our climatic conditions in four or five months and even if the same amount be taken to be oxidised on the surface of the earth in the whole year, it would mean that 5,500 million tons of carbon are oxidised every year. On a moderate estimate of 20 mgms. nitrogen fixation per gram of carbon oxidised in sunlight about 110 million metric tons of nitrogen are added to the earth by fixation

when 40% of the carbon added is oxidised. We can conclude that out of total 110 million tons at least 50% i.e., 55 million tons of nitrogen are fixed in soils by absorption of solar light. This seems to be the chief source of nitrogen added to world soils.

It is generally believed that Azotobacter are mainly responsible for this type of nitrogen fixation. Our experiments have, however, clearly demonstrated that although the amount of nitrogen fixed is double or more in presence of light than that fixed in the dark, the number of Azotobacter in light is much smaller than in the dark.

### COAL AS MANURE

We have observed that peat, lignite and bituminous coal when mixed with soil in a very finely divided condition are slowly oxidised and in this process fixation of nitrogen takes place. The amount of nitrogen fixed is greater in sunlight than in the dark. Moreover, the fixation of nitrogen by finely divided coal, lignite or peat is greatly improved when mixed with basic slag or finely divided soft rock phosphate. The estimated total nitrogen capital of the world peat and lignite is 47350 million tons. Moreover, the carbonaceous compounds present in coals are more inert than those existing in fresh plant materials and hence when finely divided coal is added to the soil, the available soil nitrogen is not readily converted into microbial protein as with freshly added plant residues. Hence finely divided coal or coal dust or coal slurry which has no use so far can be mixed with soil and basic slag or phosphate rock and crops can be grown almost immediately without giving any time interval, which is needed when plant materials are added directly to the soil.

The growing of paddy and wheat has been benefitted in our experiments by the addition of finely divided lignite and bituminous coal which add nitrogenous manures and minerals needed for the growth of crops. A mixture of coal and ammonium sulphate is a better manure than ammonium sulphate alone.

It is estimated that the nitrogen contents of humus in the top one foot of the cultivated lands of the world is 40000 million tons. The amount of nitrogen fixed in all the nitrogen industries of the world was 3.54 million tons in 1937. Hence the nitrogen, still present in the world soils in the first foot from the top is 11250 times greater than the yearly nitrogen production. It is no wonder therefore, that 3% of the world crop production has been attributed to artificial nitrogenous fertilizers.

As the world population is increasing fast the future of humanity certainly depends on an adequate and cheap supply of nitrogenous compounds for soil improvement and crop production and this has been possible by our researches which have drawn the attention of soil scientists and farmers all over the world.

# CALCIUM PHOSPHATES HELP STRAW, LIGNITE, ASSAM COAL IN FIXING ATMOSPHERIC NITROGEN IN NORMAL AND ALKALI SOILS

Some of our recent results on nitrogen fixation using straw, lignite, Assam coal with normal and alkaline soils with and without phosphates are recorded below:—

## Percent chemical composition

			Alkali soil		Garden soil
Moisture ...	...	...	1.67	...	2.14
Loss on Ignition	...	...	1.92	...	4.61
HCl—insoluble	...	...	82.094	...	77.62
Sesquioxides	...	...	9.854	...	10.2
Fe <sub>2</sub> O <sub>3</sub>	...	...	1.68	...	3.98
CaO	...	...	1.123	...	2.68
MgO	...	...	1.732	...	1.823
P <sub>2</sub> O <sub>5</sub>	...	...	0.132	...	0.192
K <sub>2</sub> O	...	...	0.7862	...	1.0678
Available P <sub>2</sub> O <sub>5</sub> (2% citric acid)	...	...	0.01642	...	0.0312
Exchangeable Ca (Hissink method)	...	...	3.8 m.e.	...	8.2 m.e.
Total carbon	...	...	0.1132	...	0.239
„ nitrogen	...	...	0.03225	...	0.0421

## Analysis of water extract of Alkali soil

Total solid	...	0.8960 %
Carbonates	...	0.1347 %
Bicarbonates	...	0.4376 %
Chloride	...	0.0302 %
Sulphate	...	0.06 %

## Analysis of energy materials used

### Percent chemical composition

	Wheatstraw	Lignite	Assam coal
Moisture	3.9	8.42	10.1
Ash content	6.84	14.72	9.9
Silica	5.08	51.2	42.98
Sesquioxides	...	3.17	32.86
CaO	0.2412	1.32	1.45
MgO	0.098	0.784	1.5
K <sub>2</sub> O	0.7025	0.421	0.82
P <sub>2</sub> O <sub>5</sub>	0.0624	0.0566	0.21
Sulphur	...	0.06	3.1
Total carbon	40.21	60.2	75.2
„ nitrogen	0.5617	0.813	1.23

## UNSTERILE

## GARDEN SOIL

Average temperature 29°

200 gms. soil+0.5% carbon as lignite

	Period in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Nitrogen fixed, lbs. per acre	Efficiency
EXPOSED	0	0.7392	0.04845	...	...	...
	150	0.6357	0.05042	0.1035	35.1	15.2
	300	0.5751	0.05127	0.1641	...	14.8
COVERED	0	0.7392	0.04885	...	...	...
	150	0.6469	0.04971	0.0923	19.2	9.2
	300	0.5979	0.05017	0.1317	...	9.3

200 gms. soil+0.5% carbon as lignite + 0.1%  $P_2O_5$  as  $Ca_3(PO_4)_2$ .

EXPOSED	0	0.7392	0.04885	...	...	...
	150	0.6151	0.05201	0.1241	70.7	25.4
	300	0.5537	0.05348	0.1855	...	25.0
COVERED	0	0.7392	0.04885	...	...	...
	150	0.6306	0.05042	0.1086	35.1	14.5
	300	0.5729	0.05116	0.1663	...	13.9

200 gms. soil+0.5% carbon as straw

EXPOSED	0	0.7356	0.04916	...	...	...
	90	0.5358	0.05329	0.1998	...	20.8
	150	0.4762	0.05441	0.2594	117.6	20.6
	180	0.4365	0.05528	0.2991	...	20.6
COVERED	0	0.7356	0.04916	...	...	...
	90	0.5866	0.05074	0.1490	...	10.6
	150	0.5417	0.05112	0.1939	43.7	10.1
	180	0.5241	0.05132	0.2115	...	10.2

200 gms. soil+0.5% carbon as straw + 0.1%  $P_2O_5$  as  $Ca_3(PO_4)_2$ 

EXPOSED	0	0.7356	0.04916	...	...	...
	90	0.4924	0.05665	0.2432	...	30.9
	150	0.4181	0.05877	0.3175	215.2	30.3
	180	0.3740	0.06024	0.3616	...	30.6
COVERED	0	0.7356	0.04916	...	...	...
	90	0.5513	0.05217	0.1843	...	16.3
	150	0.4851	0.05318	0.2505	90.0	16.0
	180	0.4652	0.05343	0.2704	...	15.8

200 gms. soil+0.25% carbon as straw+0.25% carbon as lignite

EXPOSED	0	0.7356	0.04961	...	...	...
	120	0.5587	0.05267	0.1769	...	17.3
	150	0.5329	0.05308	0.2027	77.7	17.1
	240	0.4571	0.05432	0.2785	...	16.9

UNSTERILE		GARDEN SOIL		Average temperature 29°		
200 gms. soil + 0.5% carbon as straw						
	Period in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Nitrogen fixed, lbs. per acre	Efficiency
COVERED	0	0.7356	0.04961	...	...	...
	120	0.6028	0.05083	0.1328	...	9.2
	150	0.5844	0.05097	0.1512	30.4	9.0
	240	0.5425	0.05133	0.1931	...	8.9
200 gms. soil + 0.25% carbon as lignite + 0.25% carbon as straw + 0.1% $P_2O_5$ as $Ca_3(PO_4)_2$						
EXPOSED	0	0.7356	0.04961	...	...	...
	120	0.5272	0.05560	0.2084	...	28.9
	150	0.4902	0.05668	0.2454	158.3	28.8
	240	0.4115	0.05888	0.3241	...	28.6
COVERED	0	0.7356	0.04961	...	...	...
	120	0.5740	0.05212	0.1616	...	15.5
	150	0.5410	0.05257	0.1946	66.3	15.2
	240	0.4681	0.05365	0.2675	...	15.1
200 gms. soil + 0.5% carbon as Assam coal						
EXPOSED	0	0.7392	0.05028	...	...	...
	150	0.6860	0.05115	0.0532	19.48	16.4
	300	0.6564	0.05161	0.0828	...	16.1
COVERED	0	0.7392	0.05028	...	...	...
	150	0.6956	0.05071	0.0436	9.63	9.8
	300	0.6745	0.05090	0.0647	...	9.6
200 gms. soil + 0.5% carbon as Assam coal + 0.1% $P_2O_5$ as $Ca_3(PO_4)_2$						
EXPOSED	0	0.7392	0.05028	...	...	...
	150	0.6671	0.05217	0.0721	42.5	26.5
	300	0.6301	0.05317	0.1091	...	26.4
COVERED	0	0.7391	0.05028	...	...	...
	150	0.6849	0.05114	0.0343	18.59	15.3
	300	0.6512	0.05157	0.0880	...	14.8
200 gms. soil + 0.25% carbon as Assam coal + 0.25% carbon as Straw.						
EXPOSED	0	0.7392	0.05082	...	...	...
	120	0.5551	0.05366	0.1841	...	18.4
	150	0.5212	0.05478	0.2180	28.7	18.2
	240	0.4554	0.05596	0.2838	...	18.1
COVERED	0	0.7392	0.05082	...	...	...
	120	0.6003	0.05162	0.1389	...	9.7
	150	0.5796	0.05230	0.1596	33.1	9.3
	240	0.5293	0.05268	0.2099	...	8.9

## UNSTERILE

## GARDEN SOIL

Average Temperature 29°

200 gms. soil + 0.25% carbon as Assam coal + 0.25% carbon as Straw +  
0.1%  $P_2O_5$  as  $Ca_3(PO_4)_2$

	Period in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Nitrogen fixed, lbs. per acre.	Efficiency
EXPOSED	0	0.7392	0.05082	...	...	...
	120	0.5225	0.05654	0.2167	...	29.4
	150	0.4872	0.05817	0.2520	164.6	29.2
	240	0.4051	0.06051	0.3341	...	29.0
COVERED	0	0.7392	0.05082	...	...	...
	120	0.5688	0.05297	0.1704	...	15.8
	150	0.5411	0.05393	0.1981	69.6	15.7
	240	0.4642	0.05505	0.2750	...	15.4

## ALKALI SOIL

200 gms. soil + 0.5% carbon as lignite

EXPOSED	0	0.6130	0.03898	...	...	...
	150	0.5199	0.03980	0.0931	18.3	8.8
	300	0.4690	0.04020	0.1440	...	8.5
COVERED	0	0.6130	0.03898	...	...	...
	150	0.5334	0.03937	0.0796	8.7	4.9
	300	0.4935	0.03955	0.1195	...	4.8

200 gms. soil + 0.5% carbon as lignite + 0.1%  $P_2O_5$  as  $Ca_3(PO_4)_2$ .

EXPOSED	0	0.6130	0.03898	...	...	...
	150	0.5014	0.04059	0.1116	36.0	13.5
	300	0.4438	0.04126	0.1626	...	13.5
COVERED	0	0.6130	0.03898	...	...	...
	150	0.5133	0.03974	0.0997	17.0	7.7
	300	0.4714	0.04000	0.1416	..	7.2

200 gms. soil + 0.5% carbon as Straw.

EXPOSED	0	0.6130	0.03925	...	...	...
	90	0.4242	0.04180	0.1886	...	13.5
	150	0.3697	0.04246	0.2433	71.9	13.2
	180	0.3378	0.04285	0.2752	...	13.1
COVERED	0	0.6130	0.03925	...	...	...
	90	0.4689	0.04021	0.1441	...	7.6
	150	0.4316	0.04059	0.1814	30.0	7.4
	180	0.4083	0.04076	0.2047	...	7.4



## UNSTERILE

## ALKALI SOIL

Average Temperature 29°

200 gms. soil + 0.5% carbon as Straw + 0.1 %  $P_2O_5$  as  $Ca_3(PO_4)_2$ 

	Period in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Nitrogen fixed, lbs. per acre	Efficiency
EXPOSED	0	0.6130	0.03925	...	...	...
	90	0.3987	0.04342	0.2143	...	19.5
	150	0.3372	0.04456	0.2758	118.8	19.3
	180	0.3091	0.04507	0.3039	...	19.2
COVERED	0	0.6130	0.03925	...	...	...
	90	0.4365	0.04126	0.1765	...	11.4
	150	0.3948	0.04169	0.2182	54.6	11.2
	180	0.3846	0.04189	0.2284	...	11.1

200 gms. soil + 0.25% carbon as lignite + 0.25% carbon as straw

EXPOSED	0	0.6130	0.03955	...	...	...
	120	0.4342	0.04167	0.1788	...	11.3
	150	0.4071	0.04186	0.1944	51.7	11.2
	240	0.3487	0.04248	0.2643	...	11.1
COVERED	0	0.6130	0.03955	...	...	...
	120	0.4742	0.04042	0.1388	...	6.3
	150	0.4592	0.04053	0.1538	21.9	6.3
	240	0.4146	0.04076	0.1984	...	6.1

200 gms. soil + 0.25% carbon as lignite + 0.25% carbon as Straw + 0.1%  $P_2O_5$  as  $Ca_3(PO_4)_2$ 

EXPOSED	0	0.6130	0.03955	...	...	...
	120	0.4088	0.04242	0.2042	...	16.5
	150	0.3813	0.04332	0.2317	84.4	16.3
	240	0.3235	0.04424	0.2895	...	16.2
COVERED	0	0.6130	0.03955	...	...	...
	120	0.4465	0.04121	0.1665	...	9.9
	150	0.4298	0.04132	0.1832	39.6	9.7
	240	0.3925	0.04166	0.2205	...	9.6

200 gms. soil + 0.5% carbon as Assam coal

EXPOSED	0	0.6130	0.04043	...	...	...
	150	0.5587	0.04103	0.0543	13.44	10.6
	300	0.5315	0.04128	0.0813	...	10.5
COVERED	0	0.6130	0.04043	...	...	...
	150	0.5695	0.04068	0.0435	5.6	5.8
	300	0.5449	0.04082	0.0681	...	5.6

## UNSTERILE

## ALKALI SOIL

Average temperature 29°

200 gms. soil + 0.5% carbon as Assam coal + 0.1%  $P_2O_5$  as  $Ca_3(PO_4)_2$ 

	Period in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Nitrogen fixed, lbs. per acre	Efficiency
EXPOSED	0	0.6130	0.04043	...	...	...
	150	0.5403	0.04156	0.0727	25.3	15.1
	300	0.5064	0.04203	0.1066	...	15.0
COVERED	0	0.6130	0.04043	...	...	...
	150	0.5572	0.04090	0.0558	9.1	8.4
	300	0.5241	0.04120	0.0889	...	8.6

200 gms. soil + 0.25% carbon as Straw + 0.25% carbon as Assam coal

EXPOSED	0	0.6130	0.04098	...	...	...
	120	0.4279	0.04336	0.1851	...	12.9
	150	0.3997	0.04375	0.2133	62.0	13.0
	240	0.3387	0.04446	0.2743	...	12.7
COVERED	0	0.6130	0.04098	...	...	...
	120	0.4710	0.04199	0.1420	...	7.1
	150	0.4500	0.04215	0.1600	26.1	7.2
	240	0.3889	0.04253	0.2241	...	7.0

200 gms. soil + 0.25% carbon as Assam coal + 0.25% carbon as Straw + 0.1%  
 $P_2O_5$  as  $Ca_3(PO_4)_2$ 

EXPOSED	0	0.6130	0.04098	...	...	...
	120	0.4028	0.04485	0.2102	...	18.4
	150	0.3783	0.04525	0.2347	95.6	18.2
	240	0.3120	0.04641	0.3010	...	18.1
COVERED	0	0.6130	0.04098	...	...	...
	120	0.4416	0.04280	0.1714	...	10.8
	150	0.4218	0.04302	0.1912	45.7	10.7
	240	0.3595	0.04363	0.2535	...	10.4

The foregoing results clearly show that there is nitrogen fixation not only with straw as an energy material but also with lignite and finely divided Assam coal both with normal and alkaline soils. The nitrogen fixation is much greater in presence of phosphates and in presence of light. In alkali soils the fixation is less than in normal soils because alkalies decompose the fixed N readily.

## PHOSPHATES HELPFUL IN COMPOSTING OF PLANT MATERIALS BY FIXING ATMOSPHERIC NITROGEN

We have carried on a large number of experiments on the composting of cowdung, wheat-straw, sawdust and weeds by adding only small amounts of soil in presence or absence of powdered basic slag or rock phosphate or a mixture of superphosphate and rock phosphate. We have observed a greater fixation of atmospheric nitrogen in presence of phosphates in the composting of cowdung or wheat-straw or sawdust than in their absence. Hence, a mixture of superphosphate and phosphate rock or powdered bone or phosphate rock or basic slag should be always added to compost heaps to improve the value of the composts obtained.

Some of our recent observations are recorded below :—

2.5 Kgms. wheat-straw + 1/8 soil + 32.4 lbs.  $P_2O_5$  per ton of organic matter as Rock Phosphate (Trichinopoly).

Period of incubation in days	Total carbon %	Total nitrogen %	Total carbon (gms.)	Total nitrogen (gms.)	Total carbon oxidised (gms.)	Increase or decrease of total nitrogen (gms.)	Total carbon oxidised %	Increase or decrease of total nitrogen %	C/N ratio
0	26.1	0.528	769.2	15.575	...	...	...	...	49.4
300	23.2	1.085	410.3	19.191	358.9	3.616	46.6	23.2	21.3
400	19.6	1.183	318.0	20.230	451.2	4.655	58.6	29.8	16.7
550	18.2	1.194	309.2	20.246	460.0	4.671	59.6	29.9	15.2

2.5 Kgm. wheat-straw + 1/8 soil + 32.4 lbs.  $P_2O_5$  per ton of organic matter as 1/2 Rock Phosphate (Trichinopoly) + 1/2 Superphosphate.

0	25.80	0.522	769.2	15.575	...	...	...	...	49.4
300	23.06	1.190	408.4	21.128	360.8	5.553	46.9	35.6	19.3
400	19.12	1.200	342.9	21.526	426.3	5.950	54.1	38.2	15.9
550	18.86	1.210	335.7	21.540	433.5	5.965	55.0	38.2	15.6

3 Kgms. wheat-straw + 3 Kgms. sawdust + 1/8 soil + 32.4 lbs.  $P_2O_5$  per ton of organic matter as Rock Phosphate (Trichinopoly)

0	34.70	0.560	2448.6	39.48	...	...	...	...	61.9
225	29.40	0.900	1660.0	51.00	782.6	11.52	31.9	29.1	32.6
400	26.90	1.120	1232.0	51.29	1216.6	11.81	49.6	29.9	24.0

3 Kgms. wheat-straw + 3 Kgms. sawdust + 1/8 Soil + 32.4 lbs.  $P_2O_5$  per ton of organic matter as Tata Basic Slag

0	32.00	0.515	2448.6	39.48	...	...	...	...	62.5
225	27.10	0.880	1661.7	53.60	786.9	14.12	32.1	35.7	31.0
400	25.50	1.105	1239.3	53.70	1209.3	14.22	49.3	36.0	23.0

3 Kgms. sawdust + 12 Kgms. dung + 1/8 Soil + 32.4 lbs.  $P_2O_5$  per ton of organic matter as Rock Phosphate (Trichinopoly)

0	27.30	0.863	2198.0	69.31	...	...	...	...	31.7
225	18.91	1.450	1213.6	1.81	985.4	22.50	44.8	32.5	13.2
400	16.40	1.600	926.2	90.36	1271.8	21.05	57.9	30.3	10.2

3 Kgms. sawdust + 12 Kgms. dung 1/8 Soil + 32.4 lbs.  $P_2O_5$  per ton of organic matter as Tata Basic Slag.

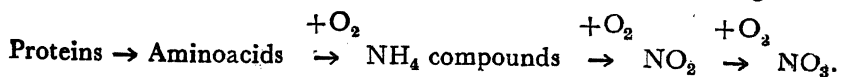
0	25.5	0.804	2198.0	69.31	...	...	...	...	31.7
225	19.10	1.400	1235.1	90.15	962.9	20.84	43.8	30.0	13.5
400	16.10	1.640	899.1	89.50	1298.9	19.19	59.4	27.6	9.8

From the balance sheet of carbon and nitrogen as recorded in the previous tables, one can readily calculate the amount of nitrogen fixed in mgms. per gram of carbon oxidised. In the following table these results have been summarised. It will be observed that the efficiency of the process of nitrogen fixation, i.e. the amount of nitrogen fixed in milligram per gram of carbon oxidised, from either sawdust or dung or leaves, singly or in mixtures, is always greater in presence of phosphates. When the same energy materials are, however, ploughed in the soil with phosphates, the nitrogen fixation is still greater. Dhar and Nagpal have observed that when 200 gms. of a good soil, containing 0.24% total nitrogen and 0.41%  $P_2O_5$ , are mixed with sawdust so that 0.5% carbon is introduced in the system with 25% moisture and allowed to undergo oxidation in air, the amount of nitrogen fixed in mgms. is 80 in light and 41 in the dark per gram of carbon oxidised. In presence of 0.2%  $P_2O_5$  as dicalcium phosphate, these values are 107 in light and 57 in the dark. Consequently, from the point of view of increase of soil fertility, direct ploughing in of plant materials or dung mixed with phosphate is certainly better than composting of plant materials with phosphates. This point of view has been clearly emphasized by Dhar in his Presidential Address to the National Academy of Sciences, India, in 1937. It is interesting to note that C/N ratio of the composts obtained in presence of phosphates is smaller than the composts prepared without phosphates.

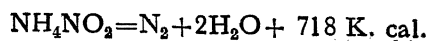
TREATMENT	Days	Efficiency
Sawdust Control	... 225	1.7
" "	... 400	0.81
Sawdust + Rock phosphate (Trichinopoly)	... 225	8.7
" " " "	... 400	4.2
Sawdust + Basic slag (Tata)	... 225	9.1
" " " "	... 400	5.1
Sawdust + Dung Control	... 225	18.8
" " " "	... 400	9.8
Sawdust + Dung + Rock phosphate (Trichinopoly)	... 225	22.0
" " " " "	... 400	16.5
Sawdust + Dung + Basic slag (Tata)	... 225	20.6
" " " " "	... 400	14.9
Sawdust + Straw Control	... 225	8.9
" " " "	... 400	5.8
Sawdust + Straw + Rock phosphate (Trichinopoly)	... 225	14.7
" " " " "	... 400	9.7
Sawdust + Straw + Basic slag (Tata)	... 225	18.0
" " " " "	... 400	11.7

TREATMENT	Days	Efficiency
Wheat-straw Control	300	4.6
" " "	400	3.7
" " "	550	3.6
Wheat-straw + Rock phosphate (Trichinopoly)	300	10.0
" " " "	400	10.3
" " " "	550	10.1
Wheat-straw + 1/2 Rock phosphate ( " )	300	15.3
" " Superphosphate	400	13.9
" " " "	550	13.5
Wheat-straw + Swedish soil Control	190	2.3
" " " "	290	...
Wheat-straw + Swedish soil + Rock phosphate (Trichinopoly)	190	6.3
" " " " "	290	3.2
Wheat-straw " " + Basic slag (Tata)	190	7.3
" " " " "	290	3.2

Under ordinary conditions the proteins present or formed in nitrogen fixation undergo ammonification and nitrification which are also accelerated by light absorption and increase of temperature and form nitrate as in the following scheme :—



In these series of reactions the unstable substance, ammonium nitrite, is formed and it decomposes according to the equation :—



Hence, along with nitrogen fixation and formation of proteins due to the oxidation of energy materials both in compost heaps or soils, ammonification and nitrification, which oppose the increase of proteins in the soil or in compost heaps, take place and, thus, the amount of protein remaining in the soil or in compost heaps, tends to decrease. Consequently, the apparent efficiency of the fixation of nitrogen, i.e. the amount of nitrogen fixed in milligram per gram of carbon of the organic matter oxidised, falls off when ammonification and nitrification take place. But, in presence of large amounts of phosphates in the system, more or less stable phosphoproteins are formed by the combination of proteins and phosphorus compounds. These compounds seem to resist ammonification, nitrification and loss of nitrogen better than proteins alone. This appears to be an important reason why the efficiency of nitrogen fixation in soils or in the compost heaps appears to be larger in presence of increasing quantities of phosphates

Our recent experiments recorded in the following Table show that when small amounts of molybdenum compounds are added to compost heaps in presence of phosphates, there is a larger fixation of atmospheric nitrogen in composts than with phosphates and organic matter :—

Straw + Soil

Balance Sheet of total nitrogen

Incubation period in days	Total carbon %	Total nitrogen %	Total nitrogen grms.	Total nitrogen increase grms.	Total nitrogen increase %
0	33.4	0.27	0.1519	—	—
90	24.3	0.60	0.1680	0.0161	10.6
150	23.1	0.64	0.1696	0.0177	11.6
Straw + Soil + Algerian rock phosphate A					
0	32.05	0.259	0.1519	—	—
90	22.0	0.570	0.1761	0.0242	13.9
150	20.5	0.675	0.1815	0.0296	16.3
Straw + Soil + Algerian rock phosphate + 0.005% molybdenum as sodium molybdate					
0	32.05	0.259	0.1519	—	—
90	16.40	0.700	0.2219	0.0700	46.0
150	15.80	0.780	0.2160	0.0641	42.2

**NITROGEN FIXATION IN THE INCUBATION OF STRAW**

Hutchinson and Richards, in their researches on the preparation of artificial farmyard manure, recorded the following observations :—

			NITROGEN			
Temperature			Loss of dry matter	Initial (mgms.)	Final (mgms.)	Loss or gain
Straw with watter	...	36°C	40.1	71	97	26
"	"	urine	26°C	49.1	507	178
"	"	"	36°C	59.8	507	176
						—329
						—331

Hutchinson and Richards could not explain the nitrogen gain in the experiments with straw alone. Some Swedish workers seem to take the view that this increase is due to the absorption of ammonia given out from the sets containing straw with urine. Dhar, in his paper on "The Role of Organic Matter in Soil Fertility" was the first to explain this increase of nitrogen with straw alone from the viewpoint of atmospheric nitrogen fixation caused by the liberation of energy evolved in the slow oxidation of cellulose and lignin of straw. In the experiments of Hutchinson and Richards with straw and urine, a large amount of urine was used and there was copious loss of nitrogen after incubation for 3 months at 26° or 36°. The carbon-nitrogen ratio of wheat straw is of the order of 56. But the carbon-nitrogen ratio in the systems of 'straw with urine' was 7.6 and, hence, a marked loss of nitrogen takes place in the incubation as observed by Hutchinson and Richards.

We have carefully carried on similar experiments with straw mixed with small amounts of urea so that the carbon-nitrogen ratios of 59.4, 58.2, 54.4 and 44.9 were much greater than 10. The results obtained by us are recorded below :—

#### Analysis of Wheat straw

Total carbon	...	36.6 %	
Total nitrogen	...	0.616 %	
			C/N ratio : 59.4 : 1
Total dry matter	...	11.4 gms.	

Incubated at 35° for 3 months

	Initial total nitrogen (mgms.)	Nitrogen after 3 months %	Total nitro- gen after 3 months (mgms.)	Increase or decrease (mgms.)	Loss of dry matter
Straw + Water	66.53	1.93	91.55	25.02	41.6
Straw + 5 mgs. urea nitrogen	71.53	2.1	93.76	22.23	39.1
Straw + 10 mgs. urea nitrogen	76.53	1.8	92.98	16.45	45.0
Straw + 24 mgs. urea nitrogen	90.53	2.3	97.92	6.39	36.1

These experiments show that in every case marked fixation of nitrogen takes place at 35° after incubation for 3 months.

From our experiments recorded in the foregoing pages and the above discussion, it is clear that for the preparation of stable composts, both calcium phosphate and lignin are useful, and, such composts can be prepared from straw, dung and sawdust and calcium phosphate with fixation of atmospheric nitrogen.

## CALCIUM-PHOSPHATE-RICH SOILS FIX NITROGEN WITHOUT ADDED ORGANIC MATTER

Moreover, in the soils containing 0.4 to 0.33%  $P_2O_5$ , we have observed a very remarkable behaviour that when these soils are allowed to undergo slow oxidation in the air, the carbonaceous matter in humus slowly undergoes oxidation both in sterile and unsterile conditions in light and in the dark, and there is appreciable fixation of nitrogen as recorded in the following table :—

### UNSTERILE

200 gms. soil in dish exposed to light for 100 days

Composition of soil :—

Temperature :

$P_2O_5$	...	0.418 %	30°—35°
CaO	...	3.402 %	
Nitrogen	...	0.2075 %	

			Initial reading %	After 100 days	Efficiency
LIGHT	Total carbon	...	1.5980	0.9581	62.5
	„ nitrogen	...	0.2075	0.2475	
DARK	„ carbon	...	1.5980	1.123	32.7
	„ nitrogen	...	0.2075	0.223	

STERILE      In test tubes containing 10 grms. soil  
After 150 days

LIGHT	Total carbon	...	1.5315	1.385	109.2
	„ nitrogen	...	0.2020	0.218	
DARK	„ carbon	...	1.5315	1.396	59
	„ nitrogen	...	0.2020	0.210	

### UNSTERILE

In dish

$P_2O_5$	...	0.3385 %
CaO	...	2.38 %
Nitrogen	...	0.044 %

After 100 days

LIGHT	Total carbon	...	0.133	0.043	45.6
	„ nitrogen	...	0.044	0.0481	
DARK	Total carbon	...	0.133	0.06	21.9
	„ nitrogen	...	0.044	0.0456	

### STERILE

In test tubes

After 150 days

LIGHT	Total carbon	...	0.135	0.12	100
	„ nitrogen	...	0.0425	0.044	
DARK	„ carbon	...	0.135	0.129	50
	„ nitrogen	...	0.0425	0.0428	



The foregoing results show clearly that soils which are rich in calcium phosphate can fix atmospheric nitrogen both in sterile and unsterile conditions when they come in contact with air and undergo slow oxidation more in light than in the dark.

### NITROGEN LOSS—A GENERAL PHENOMENON IN AMMONIA AND AMMONIUM SALT OXIDATION

For a number of years we have been carrying on extensive research work on the slow oxidation of ammonium salts and other nitrogenous compounds by air in presence of soil, sand etc. We have observed that with ammonium sulphate and other ammonium salts, there is a loss of about 60% of nitrogen more in light than in the dark. We have ascribed this loss in the nitrification of nitrogenous compounds in soil at ordinary temperature to the formation and decomposition of the unstable substance, ammonium nitrite.

On the other hand, in the industrial preparation of nitric acid from ammonia, Kuhlmann in 1839 observed that platinum was an excellent catalyst. Ostwald pushed this research further and reported that it was advisable to pass a mixture of air and ammonia as rapidly as possible over the catalyst, and that for each catalyst, there was a definite velocity at which a maximum yield was obtained. With platinum the yield of nitric acid from ammonia is 95% and this is the present industrial method. Germans have used other catalysts, but, the yield of nitric acid is smaller than with platinum.

Ammonia burns in air under the influence of catalysts and forms, in the first instance, a white fog of nitrite and nitrate. At 300° reddish brown vapours appear and with increasing temperature more and more free nitrogen and steam are produced. It has been postulated that the following reactions take place between ammonia and oxygen :—

1.  $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O} + 215.6 \text{ cal.}$
2.  $2\text{NH}_3 + 3\text{O}_2 = 2\text{HNO}_3 + 2\text{H}_2\text{O} + 153.7 \text{ cal.}$
3.  $\text{NH}_3 + 2\text{O}_2 = \text{HNO}_3 + \text{H}_2\text{O} + 80.9 \text{ cal.}$
4.  $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O} + 302 \text{ cal.}$
5.  $4\text{NH}_3 + 7\text{O}_2 = 4\text{NO}_2 + 6\text{H}_2\text{O} + 269.5 \text{ cal.}$
6.  $4\text{NH}_3 + 6\text{NO} = 5\text{N}_2 + 6\text{H}_2\text{O} + 431.6 \text{ cal.}$

According to Neumann and Rose 90% of oxidation products consist of nitrous acid when ammonia burns in air. In presence of oxygen 70 to 80% of nitric acid and 20 to 30% of nitrous acid are formed. From the very beginning of the oxidation, reaction (4) with liberation of free nitrogen takes place along with other reactions as stated above. The extent to which it occurs increases with the rise of temperature. Reaction (4) also depends on the amounts of catalysts used and on the velocity of gaseous mixture. Reaction (6) is very important as it already takes place at a temperature at which the formation of nitric oxide commences. Reaction  $(\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O} + 718 \text{ cal.})$  also gives rise to the formation of nitrogen gas. All the above reactions are exothermic and cause a rapid rise of temperature as soon as one or the other of them starts.

Ostwald attempted to increase the yield of nitric acid by the catalytic oxidation of ammonia by increasing the flow of gaseous mixture. The observations of Neumann show conclusively that the maximum yield of nitric acid by the catalytic oxidation of ammonia is obtained at a temperature of about 500°. At lower and higher temperatures more gaseous nitrogen is produced. With other cata-

lysts the production of nitrogen gas is more pronounced. Hence, in the industrial operations, even today, platinum is practically the only catalyst used.

The real clue for increasing the yield of nitric acid is to convert the whole of the ammonia into its oxidised products quickly because, when ammonia is present, it reacts rapidly with the oxidised products, nitrous acid, nitrogen dioxide and very likely with nitric acid at a high temperature.

When ammonium salts, urea, uric acid, protein, oil-cakes etc. are added to soils, the first product formed is ammonia which, in its turn, is converted into oxidised products like nitrite and nitrate. It is clear, therefore, that under these conditions, at ordinary temperature, the whole of the ammonia cannot be converted into oxidised products readily and hence ammonium ion, and occasionally free ammonia, have to coexist with nitrite ion or nitrous acid, nitrate ion and/or nitric acid, and, thus, decomposition takes place with evolution of nitrogen gas. Evolution of nitrogen gas from nitrogenous compounds in soil or in surface has to be more pronounced than in the catalytic oxidation as in the industrial process, because, oxidation of ammonia at high temperatures in the catalytic process has a larger velocity than that at ordinary temperatures in soils or in presence of sand surfaces.

There is no doubt that the loss of nitrogenous matter in soil is slowed down by addition of organic matter and, thus, crops can extract ammonium ion and nitrate under such conditions for a longer period and, hence, under ideal conditions the recovery of nitrogen, which is believed to be 50% or less, can be improved by mixing ammonium salts with organic matter. But this loss can never be stopped, because, the negative catalytic effect of carbohydrates and other substances decreases with the decrease in the concentration of such carbohydrates which are liable to be oxidised on cultivation.

We have also reported that the loss of nitrogen in the gaseous state can be minimised by mixing alkali salts or alkaline earth salts, because, in this process, a part of ammonium nitrite is converted into more stable nitrites of alkali or alkaline earth.

Recently we have observed that on adding different types of calcium phosphates to nitrogenous compounds undergoing nitrification, there is a marked retardation in the loss of nitrogen as is evident from the following tables :—

#### LOSS OF NITROGEN FROM SOILS IN LIGHT & DARK

100 gms. soil + 0.4717 gm.  $(\text{NH}_4)_2\text{SO}_4$ .

Period of exposure in days	Total nitrogen per 100 gms. of soil in gm.		Total nitrogen lost in gm.		% loss of nitrogen	
	Light	Dark	Light	Dark	Light	Dark
0	0.1436	0.1436	---	---	---	---
30	0.0724	0.1098	0.0712	0.0338	49.5	23.5
60	0.0512	0.0882	0.0924	0.0554	64.4	38.6
120	0.0468	0.0817	0.0968	0.0619	67.5	43.1

100 gms. soil + 0.4717 gm. $(\text{NH}_4)_2\text{SO}_4$ + 0.1% $\text{P}_2\text{O}_5$ as Monocalcium Phosphate						
Period of exposure in days	Total nitrogen per 100 gms. of soil in gm.		Total nitrogen lost in gm.		% loss of nitrogen	
	Light	Dark	Light	Dark	Light	Dark
0	0.1434	0.1434	---	---	---	---
30	0.1050	0.1252	0.0384	0.0182	26.8	12.7
60	0.0778	0.1128	0.0656	0.0306	45.7	22.0
120	0.0776	0.1110	0.0658	0.0323	45.9	22.5

# LOSS OF NITROGEN IN BACTERIAL NITRIFICATION

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as the source of Nitrogen

Period of Incubation : 7 weeks

Average temperature 35°

No.	Original N-content (gm.)	NH <sub>3</sub> -N left (gm.)	NO <sub>3</sub> -N formed (gm.)	Total nitrogen left (gm.)	Total nitrogen lost (gm.)	% loss of nitrogen
1	0.2565	0.1375	0.0381	0.1756	0.0809	31.56
2	0.0650	0.0096	0.0136	0.0232	0.0418	64.35
3	0.0250	0.0006	0.0031	0.0041	0.0209	83.92

(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 0.25% P <sub>2</sub> O <sub>5</sub> as K <sub>2</sub> HPO <sub>4</sub>						
1	0.2565	0.1948	0.0198	0.2146	0.0419	16.35
2	0.0650	0.0303	0.0064	0.0367	0.0283	43.63
3	0.0250	0.0095	0.0018	0.0113	0.0137	54.97

Retardation of nitrogen loss with monocalcium phosphate has been found to be 29.57 per cent whereas it is 40.58 with dicalcium phosphate and 48.19% with dipotassium phosphate.

In our experiments with different energy materials mixed with zinc oxide, aluminium oxide etc. containing no nitrogen, sand containing 0.001% total nitrogen, ordinary soil containing 0.050% nitrogen, the same soil to which urea or amino-acid has been added to raise the nitrogen content to 0.08%, the following results are obtained. These soils have not been reinforced with calcium phosphate.

Amount of Nitrogen fixed in milligrams per gram of carbon oxidised. IN LIGHT

STERILE					UNSTERILE			
Original nitrogen in the system%					Original nitrogen in the system%			
	0	0.001	0.05	0.08	0	0.001	0.05	0.08
Glucose	38	28	13	9	40	29	14	10
Cane sugar	38	27	12	8	39	28	14	10
Mannitol	37	28	12	8	40	28	13	9
Starch	40	28	13	9	40	29	14	10
Glycerol	39	28	12	9	38	28	13	9
Butter	38	28	11	8	39	29	13	9
Cellulose	40	30	14	10	41	30	13	10
Lignin	34	26	11	7	33	25	12	...
Coal	...	20	...	...	...	21	...	...

In the absence of light, the fixation of nitrogen is less than half of those recorded in the above table. The foregoing results show clearly that the efficiency of nitrogen fixation in a system depends on the amount of the available and the total nitrogen already present in the system. When these amounts are large, the formation and decomposition of the unstable substance, ammonium nitrite, in the nitrification of the nitrogenous compounds which begins soon after the formation of nitrogenous compounds by fixation, takes place readily. Hence, there is a marked loss of nitrogen from nitrogen-rich compounds, specially under aerobic conditions and the apparent fixation observed with nitrogen-rich soils mixed with energy materials appears to be small.

#### LOSS OF SOIL HUMUS BY NITRATE OR AMMONIUM SULPHATE.

In this connection, it is of interest to record that the Rothamsted soil showed a nitrogen content of 0.236% from 0.122% when farm yard manure was added at the rate of 200 tons per acre year after year and wheat grown. On the other hand, when sodium nitrate or ammonium sulphate containing 43, 86, 129 or 200 lbs. of nitrogen per acre along with adequate quantities of potash and phosphates were added to the fields and wheat grown, there was no increase in land fertility as measured by its total nitrogen content, because, the total nitrogen content, if anything, became less than the original one, i.e. 0.122%. Hence, Russell has unequivocally declared that artificial fertilizers lead to soil deterioration not only in continuous cropping but in rotations as well. Moreover, the following results obtained in Scotland and in Rothamsted show clearly that there is loss of soil humus and washing away of nitrate when large doses of ammonium sulphate or sodium nitrate are used :—

In many countries quantitative results are accumulating in favour of the view that addition of mineral nitrogen in fairly heavy doses accelerates the loss of the humus nitrogen as is evident in the observations in Rothamsted, Scotland and U. S. A.. Hall has recorded the following values of nitrates in Broadbalk in lb. per acre in wheat soils in October 1893 :—

Plot No. ....	5	6	7	8	16
	Minerals only	Minerals 43lb. N as $(\text{NH}_4)_2\text{SO}_4$	Minerals 86lb. N as $(\text{NH}_4)_2\text{SO}_4$	Minerals 129lb. N as $(\text{NH}_4)_2\text{SO}_4$	Minerals 86lb. N as $\text{NaNO}_3$
As nitrate in soil upto 90 inches	25.2	52.6	74.3	107.3	144.2
Excess of nitrate over Plot 5	...	27.4	49.1	82.1	119
Nitrogen in crop, excess over Plot 5	...	8.7	12.9	14.8	11.7
Nitrogen accounted for in soil and crop, excess over Plot 5	---	36.1	62.0	96.9	130.7
Nitrogen supplied in manure or fertilizer	...	43	86	129	86

The foregoing results show clearly that in Plot 16, 86 lb. N has been added per acre as sodium nitrate but the nitrogen existing as nitrate and that taken up by crop in excess of the plot without any nitrogenous fertilizer has the value 130.7. This result shows that about 44 lb. of extra nitrogen is coming out of the soil humus when 86 lb. N as  $\text{NaNO}_3$  is added per acre in the Rothamsted heavy soil containing about 0.122% N.

Also, the Rothamsted results show definitely that recovery of nitrogen is less than the amount added when ammonium sulphate is the fertilizer used, because, loss of nitrogen gas takes place in the process of nitrification of ammonium sulphate in the soil due to the formation and decomposition of the unstable substance, ammonium nitrite ( $\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O} + 718 \text{ k. cal}$ ), as emphasized by the workers in Allahabad, India.

J. Hendrick, in lysimeter experiments, has also reported that the amount of nitrate derived from the soil is greater in soils receiving large quantities of artificial fertilizers than in unmanured soils. The amounts in lb. of ammonium sulphate per acre over a period of 15 months are :—

	No fertilizer	$(\text{NH}_4)_2\text{SO}_4$ added + N	$(\text{NH}_4)_2\text{SO}_4$ (superphos- phate) + N	$(\text{NH}_4)_2\text{SO}_4$ + superphos- phate + KCl + N
Total nitrate in crop and drainage water	193	774 (175)	792	776
Nitrate supplied by fertilizer	...	475 (107)	475	475
Nitrate from soil	...	299 (67.6)	317	301 (67.8)

It can be concluded here also from the foregoing results that the addition of about 100 lb. nitrogen per acre as ammonium sulphate alone or with superphosphate or with superphosphate and potassium chloride, there is marked depletion of humus nitrogen and loss of soil fertility as a permanent measure. This can be avoided by adding farm yard manure, straw, leaves etc. along with the artificials. It is evident that the depletion of humus nitrogen is actually greater than the amounts recorded in the above tables because of the loss of nitrogen as nitrogen gas on adding ammonium sulphate.

Due to the introduction of tractors and other machines in modern agriculture farm manure is not available as much as desirable for maintaining and improving soil fertility permanently. Hence more and more artificial nitrogen is being used in Europe and U. S. A. Man has always utilised the humus created by trees in forests and by grass in his agriculture and he early found that animal dung is quite good for his crop and used it, chiefly for production of his crop till the beginning of the present century. At present the farmers are using larger quantities of artificial nitrogen than before, but, the above results and the Woburn studies lasting for 80 years and Rothamsted observations continued for 110 years force us to the conclusion that artificials even in heavy doses cannot maintain soil fertility but frequently deplete the soil humus which is an excellent and steady supplier of plant nutrients. Hence, for a steady crop production and maintaining soil fertility, farm

yard manure, straw, plant residues etc. should be added in larger amounts aided by calcium phosphate for increasing the nitrogen fixation in soil and its humus content. When artificials have to be used in modern agriculture, the amount should always be less than about 100 lb. nitrogen per acre as larger amounts may cause depletion of humus nitrogen as recorded in the Rothamsted, and Scottish experiments noted in the foregoing pages. It has been reported that 120—150 lb. N as artificials per acre for growing corn in U. S. A. and 150—200 kg. of N as  $(\text{NH}_4)_2\text{SO}_4$  per hectare in France are being used, but, such heavy doses are likely to cause humus loss.

Moreover the yield of barley and wheat in Rothamsted experiments was greater and uniformly steady with farm yard manure than with artificials. On adding farm yard manure, the total nitrogen of the fields went on increasing from 0.122% to 0.256% along with the increase in soil humus and this increase of nitrogen and humus led to the steady liberation of greater amounts of available nitrogen, phosphate, potash and trace elements and thus the yield of crops from the farm yard manure plot was greater than from the fields fertilized by artificials.

In Rothamsted, on an average, the addition of one ton of farm yard manure produced an increase of 0.13% nitrogen. In the Woburn experiments, the nitrogen increase for a ton of manure was 0.09%. Using 6 tons of manure for 50 years, the Missouri Experiment Station obtained an increase of 41.1% in the total nitrogen in the soil. Hence, as 300 tons of manure were added, an increase of 0.137% was observed per ton of manure added. Similarly, in the Askov experiments, 30% increase of total nitrogen has been observed in the farm yard manure plots. The Rothamsted experiments show clearly that the gain in total nitrogen on the addition of farm yard manure to the land was more marked in the early years than in later periods. This cannot be attributed, as is generally done, only to the retention of the nitrogen added in the form of farm yard manure. The original soil nitrogen in Rothamsted was approximately 0.122% in 1843 when the manuring experiments were started. In the first 22 years, there was more marked increase of soil nitrogen (46%) than in the next 28 years (21%). If the retention of the added nitrogen were the only cause of the increase of total nitrogen in soil as observed experimentally, this behaviour should have been more marked in the later period of the experiments when the total nitrogen content of the soil became high. It is well known that when organic matter is added to the soil of low humus content, the added organic matter is oxidized rapidly in the beginning leading to fixation of atmospheric nitrogen, and, in a short time, the nitrogenous substances present in the soil and those produced by fixation of atmospheric nitrogen undergo nitrification and loss.

#### BASIC SLAG AND ORGANIC MATTER PROFITABLE IN LAND IMPROVEMENT

It is interesting to record here that the percentage of total nitrogen in our fields at Allahabad rose from 0.0368% to 0.094% after the first application of cow dung and when the C/N ratio of the system became 10 : 1. On the second addition of cow dung the nitrogen status became 0.1517% and rose to 0.200% after the third application of the dung. The three doses were added in 3 years. The corresponding results with Neem leaf (*Melia Azadiractta* Lina) are as follows :—

Original nitrogen content of the soil.....	0.0386%
After first application.....	0.0628%
After second application.....	0.0815%
After third application.....	0.1021%

The foregoing result show conclusively that repeated applications of cow dung and leaves of Neem enrich the soil markedly by increasing its nitrogen and humus by fixing atmospheric nitrogen and also by retaining partially the nitrogen of the material added.

By adding municipal wastes to a land in front of the Sheila Dhar Institute of Soil Science, University of Allahabad, containing 0.04% total nitrogen, the total nitrogen content was raised to 0.25% in course of 4 to 5 years and bumper crops were obtained. This land had animal bones mixed with it.

Recently, we have added basic slag in small lumps to a field of the Sheila Dhar Laboratory to which municipal waste was dumped for about a year. When the samples of this soil were analysed, the following results were obtained :—

	Total carbon %	Total nitrogen %	C/N ratio
1. No phosphate ...	1.90	0.172	11.0
2. Tata basic slag ...	1.766	0.331	5.3
3. Do. ...	2.01	0.270	7.4
4. Do. ...	1.89	0.279	6.7

The foregoing results clearly show that with all types of organic matter, mixed with basic slag or bone, land fertility can be enormously increased.

Our experimental results obtained with dung and phosphates show clearly that the nitrogen fixation observed with dung is much greater in presence of phosphates than in their absence. Consequently, the nitrogen increase recorded by adding farm yard manure in different Experimental Stations would have been much greater if the farm yard manure were incorporated with basic slag or powdered phosphate rock or superphosphate before its incorporation in the soil. From our researches we are convinced that all over the world in composting farm yard manure or its ploughing directly into the soil, addition of basic slag or powdered phosphate rock or superphosphate seems indispensable for permanent land improvement and agriculture.

#### PHOSPHATE HELPFUL IN FORMATION OF NITRE BEDS

In previous papers Dhar advanced a theory explaining the formation of natural nitre beds in Chile and other parts of the world based on the phenomenon of nitrogen fixation aided by sunlight. It has been reported that phosphates exist in the overlying rocks near deposits of Chile salt-petre. From our experiments we have observed that when calcium phosphates are mixed with all types of organic matter undergoing oxidation, there is marked fixation of atmospheric nitrogen and formation of proteins, aminoacids and ammonium salts. This fixation of nitrogen by the slow oxidation of organic matter is much greater in presence of light than in its absence, and, actually light is utilized in producing more nitrogenous compounds. Moreover, in the presence of calcium phosphates, the nitrogen fixation is much accentuated.

Hence, all types of organic substances, like sea-weeds, planktons, when mixed with guano or bird deposits or bones of fish or animals rich in calcium phosphate,

fix atmospheric nitrogen copiously specially in presence of sunlight. These nitrogenous compounds in course of time can undergo nitrification more in light than in the dark and can be converted into nitrates of sodium, potassium, calcium, magnesium etc.

We have observed that when potassium salts, sodium salts or soluble calcium or magnesium salts are mixed with nitrogenous substances undergoing nitrification, the formation and decomposition of the unstable substance, ammonium nitrite which is always produced in the nitrification of nitrogenous compounds, is decreased due to the formation of nitrites of the alkali and alkaline earth metals. Consequently, formation of nitre beds may be due to the photochemical, catalytic and bacterial nitrification of the nitrogenous compounds obtained from weeds, planktons, animal bodies and those fixed in the slow oxidation of organic substances with carbon-nitrogen ratios greater than 10 aided by calcium phosphates derived from sea animals, fishes, dungs of birds and animal.

It is quite possible that under certain conditions the soluble nitrates thus produced may be separated from the calcium phosphate by washing down from the highlands and accumulated by the evaporation of water in the valleys. That sea water and sea-weeds and materials present in sea beds play an important role in nitre bed formation is clear from the following composition of an average sample of caliche which contains many chemicals present in sea water and beds :—

	Per cent
Sodium nitrate ( $\text{NaNO}_3$ )	... 8— 25
Potassium nitrate ( $\text{KNO}_3$ )	... 2— 3
Sodium chloride ( $\text{NaCl}$ )	... 8— 25
Sodium sulphate ( $\text{Na}_2\text{SO}_4$ )	... 2— 12
Calcium sulphate ( $\text{CaSO}_4$ )	... 2— 6
Magnesium sulphate ( $\text{MgSO}_4$ )	... 0— 3
Sodium baborate ( $\text{Na}_2\text{B}_4\text{O}_7$ )	... 1— 3
Sodium iodate ( $\text{NaIO}_3$ )	... 0.05— 0.1
Sodium perchlorate ( $\text{NaClO}_4$ )	... 0.1— 0.5
Insoluble matter	... 23— 70

#### PRACTICAL RESULTS OBTAINED WITH CALCIUM PHOSPHATE IN CROP GROWTH IN MANY COUNTRIES

The Americans seem to be doing a great service unknowingly to their soils by adding an overdose of phosphate because the phosphate, raised upto 0.2% i.e. 5000 lbs. per acre aided by the leaves, roots and other plant residues, farmyard manure etc., can certainly enrich the soil from the nitrogen point of view. On page 170 of Collings' book "Commercial Fertilizers" (1947 ed.) and in figure 58, a better growth of wheat has been shown when crop residues are mixed with rock phosphate and ploughed in, in comparison with only crop residues ploughed in. This is exactly what should be done in temperate countries in acidic soils where even 5 tons of straw per acre should be ploughed in along with calcium phosphate or basic slag, but not superphosphate. On pages 170-171 Collings has reported as follows :—



"The Illinois Experiment Station has probably had more practical experience with the use of phosphate rock than any other agricultural experiment station in the world. Because of the cheapness of the phosphate rock as compared with other carriers of phosphorus, the Illinois Experiment Station has conducted a very active propaganda in its favour. They recommend that 1000 to 2000 pounds of the phosphate rock be applied once every 3 or 4 years, or once during a rotation until the phosphoric acid content of the soil has been raised to about 5000 lbs. per acre. It should be maintained at this level. They also recommend that the phosphate rock be ground to such a fineness that it will pass through a sieve having 100 meshes to the linear inch, or about 10000 meshes to the square inch. They advise that the phosphate rock be broadcast and preferably turned under with a green manuring crop. If lime is to be applied for the same crop, they recommend that it be broadcast and harrowed into the surface layers of the soil after ploughing under the phosphate rock".

It is generally accepted in U. S. A. that when the price of superphosphate is twice as much per ton as the price of phosphate rock, it may be profitable to use phosphate rock rather than superphosphate. Tennessee Experiment Station has obtained favourable results from the use of ground phosphate rock in the first year following the application. It appears that phosphate rock materially adds in the building of the phosphate reserve in the soil.

The unbalanced character of stable manure as fertilizer has long been recognised. It contains too much nitrogen in proportion to its  $P_2O_5$  content. The addition of phosphate to the manure increases its value as shown in the following table. In this experiment phosphate rock or superphosphate was mixed to the manure and applied to on red clover sod which was ploughed under for growing corn in a rotation with wheat and red clover. Manure was applied at the rate of 8 tons per acre and phosphate rock, superphosphate or gypsum at 40 lbs. per ton of manure :—

TREATMENT	Comparative effects of phosphate rock and superphosphate when applied with manure			
	26 year average acre yields			
	Corn (bu.)	Wheat (bu.)	Clover (cwt.)	
Superphosphate and manure	... 67.7	28.5	48.97	
Phosphate rock and manure	... 67.4	27.3	46.75	
Gypsum and manure	... 63.6	25.3	40.71	
Manure alone	... 61.8	23.8	41.51	
Unfertilized	... 36.7	14.1	29.37	

On page 400 of "Soil Science" by W. W. Weir, it has been stated as follows:—

#### REINFORCING MANURE WITH PHOSPHATE

Thorne (1907) and other investigators have found that when manure is reinforced with from 25 to 40 lbs. of superphosphate or from 40 to 80 lbs. of rock phosphate per ton, its fertilizing efficiency is greatly increased, specially on soils that are deficient in available phosphorus.

## PHOSPHATES AS PARTIAL SUBSTITUTES FOR NITROGEN FERTILIZER

F. E. Bear, in his "Soils and Fertilizers" (1942), has stated as follows on pages 291-292 :—

"Within limits phosphate fertilizers together with potash salts and lime can be substituted for nitrogen fertilizers. Their use stimulates the nitrogen fixing bacteria, both symbiotic and non-symbiotic, to greater activity. The rank growth of white clover that follows on the addition of phosphate and potash resembles the application of nitrogenous fertilizers."

"The value of phosphate and potash fertilizers and of lime as agents to stimulate nitrogen fixation is greater for annual or biennial legumes in crop rotations. In the growing of perennial legumes—like alfalfa—a difficult problem is presented in trying to supply adequate amounts of phosphate to meet the needs of these legumes for the continuous growth. Excessive fixation occurs if heavy applications of phosphate are made in advance of seeding and top dressing applications of phosphate are made after the crop started, the result is not effective. The only practical method of dealing with this problem is to plough up the legume from time to time and re-seed."

"There is no atmospheric supply of phosphorus. The quantity in the soil is relatively small. In proportion as crops and live stocks are sold from the farms the element phosphorus is carried off with them. This loss must be compensated for by the use of phosphate fertilizers. Phosphorus is the predominating element in the fertilizers that are used on the grain crops. Phosphate fertilizers are specially important in the production of roots, cereals and clovers. They hasten the maturity of the crop. They are useful in precipitating aluminium in acid soils".

On page 284 the following is stated :—

"In strongly acid soils the phosphate rock is more effective than when the reaction of the soil is approximately neutral. This is shown in the following table :—

Acre yields with use of Superphosphate and Phosphate Rock. (Wiancke)

P H O S P H A T E	C O R N    W H E A T				C L O V E R	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	Bu.		Bu.		cwt.	
Superphosphate	27.9	26.5	11.5	14.3	13.8	19.5
Rock phosphate	31.8	28.0	16.3	12.1	19.5	19.9
S. P. complete fertilizer	37.8	38.9	14.5	16.5	19.5	22.6
R. P.    "    "	39.0	37.8	18.5	14.6	23.4	24.0
S. P. and manure	44.6	45.7	19.0	18.2	22.8	23.7
R. P.    "    "	44.5	44.5	21.0	18.4	27.4	24.9
No fertilizer	21.9	25.3	4.8	7.6	9.0	12.5

It has been recently stated that many soils are deficient in their phosphate content. The phosphate content of the soils analysed by us show that our soils are not poor in their phosphorus content. In the table recorded below the  $P_2O_5$  content in the first foot of the soils is practically constant and is approximately 0.112%.

Percentage composition of CaO, MgO,  $K_2O$  and  $P_2O_5$  in the first and second foot of the soils.

		CaO %	MgO %	$K_2O$ %	$P_2O_5$ %
1. FALLOW LAND	1st foot of soil	0.6863	0.9668	0.1872	0.1186
	2nd " "	0.9339	1.1406	0.2012	0.1242
2. SUNHEMP OR SANAI	1st " "	0.3750	0.7930	0.5133	0.1137
	2nd " "	0.4125	0.7505	0.5092	0.0982
3. PULSES	1st " "	3.0100	1.7208	0.5351	0.1117
	2nd " "	3.6400	1.6495	0.3976	0.0939
4. LUCERNE	1st " "	2.1248	1.2340	0.5212	0.1128
	2nd " "	2.5440	1.1552	0.4028	0.0946

PHOSPHATE STATUS OF TEMPERATE COUNTRY SOILS IS INFERIOR TO THAT OF ALLUVIAL TROPICAL SOILS DUE TO ACIDITY AND SLOW WASHING.

On the other hand, the phosphorus content of the American soils recorded by Bear on page 48 of his book "Soils and Fertilizers—1942" varies from 0.04—0.29% of  $P_2O_5$ .

Russell and Voelcker, in their book "Fifty Years of Field Experiments at the Woburn Experimental Station, 1936," have recorded the following results on the Woburn and the Rothamsted soils.—

#### PHOSPHORIC ACID EXTRACTED FROM WOBURN & ROTHAMSTED SOILS

Mgs.  $P_2O_5$  per cent .....

(L. A. Dean's data)

	Plot	Inorganic Alkali soluble	Inorganic Acid soluble	Total by fusion
WOBURN BARLEY 1927				
No manure	1	40	11	160
Minerals only	4	70	37	250
{ Minerals and Sulphate of ammonia	5a	110	24	250
Farmyard manure	11b	65	23	240
ROTHAMSTED WHEAT				
No manure	3	7	40	140
Minerals only	5	9	170	290
{ Minerals and Sulphate and ammonia	8	9	130	260
Farmyard manure	2b	13	130	300

It has been frequently stated that Rothamsted soil is less acidic than the Woburn soil. The results recorded in the above table show that at Rothamsted most of the added phosphate remains in an acid soluble form and is readily available to crops. On the other hand, at Woburn, the greater part of the added phosphate appears to be present as ferric or aluminium phosphate and not easily available to crops. Moreover, on the addition of farmyard manure at 14 tons per acre to the Rothamsted soils the nitrogen status of the soils was greatly enhanced. But on adding artificial nitrogen no marked improvement in the nitrogen status took place as is evident in the following table :—

*Page 284 of "Soil Conditions & Plant Growth" by E. J. Russell, 1950*

The original nitrogen present in the soil is believed to be 0.122%

Nitrogen percentage in the top 9 inches of Broadbalk Soils

Plot	3	5	7	2A	2B
				FARMYARD	MANURE
Manure	None	PK	NPK	Since 1885	Since 1843
1865	0.105	0.106	0.117	—	0.175
1881	0.101	0.107	0.121	—	0.184
1893	0.094	0.101	0.115	0.136	0.213
1914	0.093	0.103	0.115	0.191	0.236
1936	0.103	0.105	0.120	0.186	0.226
1945	0.105	0.136	0.123	0.194	0.236

On the other hand, in Woburn where the soils are acidic and not heavily limed, even on adding farmyard manure at 8 tons per acre, there was only a small increase in the total nitrogen content specially in the early years of the experiments, as is evident in the following table :—

Nitrogen as Percentage of Air-dry  
Surface Soil in the permanent  
Wheat and Barley Plots. (A. Walkley's data).

INITIAL VALUE IN 1876: 0.156 PER CENT

Manuring PLOTS		Farmyard manure 11b	Nitrate of Soda 3,6,9	Sulphate of ammonia 2,5,8	No nitrogen 1,4,7	Mineral manures 4,5,6	No mineral manures 1,2,3
Date	Crop						
1888	Barley	0.160	0.142	0.139	0.131	0.132	0.143
1888	Wheat	0.171	0.130	0.136	0.134	0.129	0.128
1898	Barley	...	0.120	0.121	0.123	0.112	0.127
1898	Wheat	...	...	0.126	0.129	0.124	0.132
1927	Barley	0.151	0.107	0.100	0.092	0.099	0.100
1927	Wheat	0.145	0.102	0.103	0.112	0.107	0.101
1932	Barley	0.123	0.100	0.095	0.091	0.097	0.097
1932	Wheat	0.124	0.099	0.099	0.108	0.103	0.100

This great difference in the behaviour of the Rothamsted and the Woburn soils seems to be due to the more marked fixation of nitrogen in the more neutral and calcium carbonate rich soils of Rothamsted than in Woburn. The phosphates present in the Rothamsted soils are available (phosphates of calcium and magnesium) for the purpose of increased fixation of nitrogen whilst the phosphates in the Woburn soils are mainly in an unavailable condition (phosphates of Fe, Al and Ti) and, hence, are not helpful to nitrogen fixation due to the addition of farmyard manure.

It is interesting to note that the drainage water in Rothamsted, Broadbalk field contains 1.54 parts of  $P_2O_5$  per million of water when the fields are treated with complete artificials whilst the unmanured field contains 0.6 p.p.m. It appears, therefore, that appreciable amounts of phosphate may be slowly washed away from temperate country soils by rain.

Similarly, the  $P_2O_5$  and  $K_2O$  contents of some Danish soils, as recorded in "Forsøg med Stadgodning og Kunstgodning Ved Askov. 1894-1948" and "Ved Karsten Iverson og K. Dorph-Peterson", are as follows :—

Page 466.

				Unmanured	Artificial fertilizer	Farmyard manure.
$P_2O_5$	...	1923	...	0.052 %	0.072 %	0.064 %
		1930	...	0.049 %	0.066 %	0.066 %
$K_2O$	...	1923	...	0.089 %	0.099 %	0.098 %
		1930	...	0.083 %	0.090 %	0.094 %

The above results were obtained with a loam soil of Askov whilst a sandy field of Askov gave the following percentages of phosphorus and potash :—

Page 473.

				Unmanured	Artificial fertilizer	Farmyard manure
$P_2O_5$	...	1923	...	0.076 %	0.083 %	0.084 %
		1930	...	0.074 %	0.082 %	0.083 %
$K_2O$	...	1923	...	0.053 %	0.057 %	0.057 %
		1930	...	0.053 %	0.055 %	0.057 %

The rainfall of Askov is rather uniform and varies from 34—63 mm. per month. It appears, therefore, that in such wet and temperate countries an appreciable amount of phosphate and potash are washed away. Hence, these values are smaller than those obtained by us with Indian soils.

[ Sir A. D. Hall, in his book "An Account of the Rothamsted Experiments, 1905, has stated as follows regarding the Rothamsted soils :—

"There is an abundant stock of potash. A complete mineral analysis in which the Broadbalk soil was completely broken up by  $H_2F_2$  yielded 2.26% of potash, four times the amount that can be extracted by long digestion with HCl. In phosphoric acid the soil is by no means so rich. The unmanured plots contained in 1905 less than 0.1%; the highest limit reached in the heavily manured plots was 0.25%. Under ordinary farming conditions the soil shows no particular need of phosphoric acid as do many clay soils".

On page 479 Sir John Russell, in his book "Soil Conditions & Plant Growth, 1932, has stated as follows :—

"Phosphorus is peculiar in that some soils are notably deficient in it; these occur commonly in Australia and South Africa, but also in the United Kingdom. in consequence the vegetation is affected and the grazing animals suffer serious phosphate starvation". Again, on page 554 he has stated : "Phosphate exhaustion was the most serious occurrence because there was no way of meeting it, and, as the original supplies were not as a rule very great, it must have been acute by the end of the 18th. century in England, for, remarkable improvements were and still are effected all over the country by adding phosphates. Then began a process, which has gone on to an increasing extent ever since, of ransacking the whole world for phosphates; at first the search was for bones, even the old battlefields were not spared if we may believe some of the accounts that have come down; later on (in 1842) Henslow discovered large deposits of mineral phosphates to which more and more attention has been paid. Phosphate supplies may yet become the factor that will determine the course of history".

Similarly, F. G. Clarke (The Data of Geochemistry Department Institute U. S. Geological Survey Bulletin 770, 1924) has reported that the potash content of humid soils of U. S. A. is 0.216% and in arid soils it is 0.729% whilst the  $P_2O_5$  content is 0.113% and 0.117% respectively.

The following tables show that in many American soils the phosphate ( $P_2O_5$ ) is even smaller than the total nitrogen content and is much smaller than the potash ( $K_2O$ ) content :—

Table 3, page 61 from "Farm Soils, Their Management and Fertilization" by E. L. Worthen, 1948.

POUNDS OF TOTAL PLANT FOOD  
IN 2,000,000 POUNDS OF SOIL

Description of Soil	Location	Nitrogen	Phosphoric acid ( $P_2O_5$ )	Potash ( $K_2O$ )	Lime (CaO)
Limestone valley	Pennsylvania	...	2,400	2,300	69,600
Residual (shale)	West Virginia	...	2,750	1,624	26,400
Glacial (limestone)	New York	...	4,800	3,220	40,440
Glacial (shale)	New York	...	5,200	2,732	44,616
Coastal plain	New Jersey	...	1,300	3,119	18,836
Maryland barrens	Maryland	...	..	414	2,400
Piedmont plateau	North Carolina	...	790	1,288	55,440
Coastal plain sand	South Carolina	...	759	867	11,992
Timbered glacial soil	Ohio	...	1,860	2,116	4,756
Gray prairie	Illinois	...	2,777	1,868	30,798
Brown Prairie average	Iowa	...	5,458	3,209	34,490
Fest (1,000,000 lbs.)	Wisconsin	...	33,900	3,611	5,820
Upland Brazos Co.	Texas	...	1,620	695	15,518
Gray timber soil	Missouri	...	2,800	2,530	41,821
Prairie	Kansas	...	2,800	1,686	19,716
Residual limestone	Kentucky	...	...	1,895	32,063
Black Prairie (glacial)	North Dakota	...	6,335	3,050	31,100

In unmanured Danish soils also the  $P_2O_5$  content is low, i.e. 0.052% and when farmyard manure is added, it goes up to 0.064%. Similarly, O. Frank (Vaxt Narungs NYTT Noz, 1946, pages 8-12) has stated that the majority of the Swedish soils are clearly deficient in phosphate. Moreover, G. Tommassi and L. Marimpietri (Extr. des Annali Sper Agraria, Vol. XI; 1941, Rome) have emphasised that phosphorus is the principal factor in crop production and that  $P_2O_5$  content of most soils in Italy is low. Dr. A. De Dominicis of Naples has reported as follows :—

“The Chemical Station of the Agricultural Research Station at Rome has established that about 15 to 30 kilograms of assimilable phosphate are necessary per hectare of land for a proper crop yield”.

The problem of the supply of potash to the arid soil in Italy is less important than that of phosphate because most of the Italian soils have a fair amount of potash. Moreover, in South Africa it has been reported that phosphates are the only form of fertilizer which may be expected to give fairly constant return under acid conditions.

Dr. Nervos has stated that the dry soil in Greece is poor in nitrogen and phosphorus but fairly rich in potash and lime.

In French Morocco, Dr. Miede has stated that phosphorus plays a most important part but its efficacy frequently depends on the presence of organic matter and lime.

Dr. Prescott of Australia has always emphasised on the need of Australian soils for the supply of phosphates. He has reported that owing to the low phosphate status of most dry soils in Australia, the nitrogen status in virgin soils is exceptionally low.

Thus, it appears that in most countries the normal soil contains 0.1% or less  $P_2O_5$  and thus deficient in phosphate.

#### WHY GRASSLAND IS RICHER IN NITROGEN THAN FOREST OR TIMBER LAND ?

In my paper on “Importance of Organic Manures and Inorganic Fertilizers” (Proc. Nat. Acad. Sc. 1951, 20, p. 151-192) it has been stated that “prairie soils or those covered with grass are richer in their humus and nitrogen contents than timber soils. This may be due to the fact that more sunlight falls on grasslands and helps in the improvement of nitrogen status by the fixation of atmospheric nitrogen from the oxidation of carbonaceous compounds than forest or timber soils”.

There is another valuable reason of this important phenomenon. It has already been stated that the ratio of Ca : P in leaves of trees is 14.1 whilst the Ca : P of wheat straw is 2 : 1. This is a very interesting fact, that the phosphate content of the tree leaves in comparison to calcium is much smaller than in wheat or oat straw. It appears, therefore, that the calcium phosphate status of forest or timber soils is lower than that of grass soils. The various Bulletins of the University of Alberta, Canada, on soil survey bring out this point very clearly showing that the calcium phosphate contents of the profiles of wooded soils are appreciably smaller than those of open grass lands. Odynsky and Newton, in Bulletin No. 53 (1953), Report No. 15, Alberta Soil Survey, have stated on page 75 : “The phosphorus content of the surface foot varies from an average of 0.08% in the black soils to an average of 0.035% present in the gray wooded soils”.

Calcium phosphate has been found to be able to help nitrogen fixation in soils very considerably. Hence, the nitrogen and humus status of forest soils is inferior to that of grass or prairie soils.

Addition of powdered phosphate rock or basic slag is bound to improve the fertility of forest soils which are usually highly acidic and this should be adopted specially in temperate countries. Generally there is more leaching of forest soils which are more acidic than grass soils where the leaching is less than forest soils.

#### C/N RATIO OF ACIDIC SOILS MUCH GREATER THAN THAT OF NEUTRAL & ALKALINE SOILS

It is certain that liming or the addition of calcium phosphates decrease the acidity of soils and favour the oxidation of organic substances present therein. It is well known that the carbon/nitrogen ratio of soils increases with their acidity. On the other hand, we have repeatedly observed that the carbon/nitrogen ratio of alkali soils is much smaller than 10. Frequently, this ratio in the alkali soils of India having a pH value of 10.7 is 3. In other words, the percentage of nitrogen present in the humus of the soil depends on the pH of the soil. The greater the pH, the greater is the percentage of nitrogen present in the humus of the soil. Hence, it can be inferred that on adding lime or calcium carbonate or calcium phosphate to an acid soil, not only the acidity decreases but also the carbonaceous matter undergoes more rapid oxidation and the energy obtained in this oxidation fixes nitrogen of the atmosphere in the soil. Thus, the carbon/nitrogen ratio of the acid soil decreases and its fertility increases, specially by the addition of calcium phosphate or basic slag which markedly increases the nitrogen fixation in the oxidation of organic matter. These conclusions are supported by the properties of fen soils. Russell has reported that when the vegetation includes calcicolous (calcium-rich plants), the neutral humus soils in which the oxidation of the organic matter is rapid, are formed. The chief characteristics of these fen soils are their richness in lime and high nitrogen content. When drained, these fen soils prove highly fertile. The soil water is not acid but contains calcium bicarbonate. These soils contain calcium carbonate and calcium phosphate and, hence, can fix atmospheric nitrogen readily by oxidation of the organic matter, and, that is why they are rich in nitrogen. They do not require nitrogen or lime but respond to phosphates.

We are definitely of the opinion that both, calcium carbonate and calcium phosphate, should be used as soil improvers. Phosphate rocks or basic slag in a finely-divided condition should not only serve as a soil amendment but can enrich the soil by helping nitrogen fixation caused by the oxidation of organic matter.

Collings, in his book "Commercial Fertilizers", has stated on pages 393-394 as follows :—

"Low crop yields are more often due to a lack of phosphoric acid than to the lack of any other nutrient. Phosphoric acid has often been called the 'master key' to agriculture. Phosphoric acid appears to be concerned in the production of nucleoproteids, and it appears that phosphoric acid influences the production of seed or grain more particularly than does nitrogen or potash".

Moreover, Collings has also stated on page 194: "In all probability the major portion of the cultivated soils of the U. S. A., east of the Mississippi river, would be forced out of crop production within a comparatively few years if phosphate fertilizers were withheld". He has also recorded on pages 338-339: "East of the one hundredth meridian are found soils whose pH value generally lies between



5.0 and 6.0, although, pH values of 4.5 or 4.0 are not uncommon". In general, it might be said that the acidity of the cultivated soils of the U. S. A. increases from the Gulf of Mexico to the Canadian border as does also their nitrogen and organic content.

From our researches on the marked increase of nitrogen fixation in the oxidation of organic substances aided by calcium phosphate we are convinced that the addition of finely-divided calcium phosphate or basic slag would lead to marked nitrogen fixation and increased fertility not only to the acid soils of the world, but, also to the peaty and organic soils found in Europe and America. In such soils, the addition of calcium phosphate or basic slag will certainly be more profitable for crop production than liming.

In experiments carried on in Belgian Congo, maize showed large immediate and residual response to "hyper phosphate Reno," which is a finely powdered Gafsa rock phosphate.

In East Africa natural Uganda rock phosphate and this material heated with soda ash produced favourable results in grain crops where the rainfall is adequate. Moreover, dung was found to be better than artificial fertilizers and animal manure shows prolonged residual effect but not N and P fertilizers.

It has been reported that in some of the States of the Pacific side of U. S. A. such as Washington, Oregon, Nevada, Montana, Idaho, Wyoming, Utah, Colorado, the soils are rich in  $P_2O_5$  (0.2 to 0.3%). The States round about Florida are poor in phosphate (0 to 0.4%). It seems clear from our researches that for maintaining and improving the fertility of these Southern States large doses of organic matter fortified by calcium phosphate or powdered phosphate rock or basic slag should be of great value. The States on the Pacific Coast, however, can be improved from the nitrogen point of view by the addition of organic substances alone as they are already rich in phosphate.

From a survey of the nitrogen and phosphorus status of world soils, it appears that generally in temperate country soils the N : P ratio is about 3 to 4 whilst this ratio is smaller in tropical soils.

#### PHOSPHATE RICH SOILS CONTAIN MORE NITROGEN THAN PHOSPHATE POOR SOILS.

*Nitrogen/Phosphorus ratios in West Virginia Dekalb soils.*  
(15 years of experimentation. All crops removed).

PLOT	Fertilizer treatment		Hundred-weight produce per acre in 15 years	Pounds per two million of soil		N : P ratio
				Phosphorus	Nitrogen	
25	Manure	...	1396	1220	3240	2.65
20	M-Ca	...	1524	1050	2700	2.57
26	N-P-K	...	1179	900	2660	2.95
31	N-P	...	959	880	2400	2.72
34	P	...	634	880	2300	2.61
28	P-K	...	769	860	2280	2.65
19	N-P-K-Ca	...	1206	740	2130	2.88

It is evident that the nitrogen/phosphorus ratio in the soil remained fairly constant irrespective of differences in fertilizer treatments or in the amounts of crops removed. Phosphorus apparently is related to nitrogen fixation or to nitrogen conservation, one or both. Consideration of the nitrogen content of the crops removed led to the conclusion that nitrogen fixation estimated at from 20-75 lbs. per acre per year had taken place in the soil of these plots, the higher amount having been calculated in the case of the plots receiving both superphosphate and sulphate of potash.

“ The only correlations with the nitrogen content which have been established are those of the content of P and of organic matter in soils of the same type and under similar climatic and cultural conditions.”

In the following table similar results obtained by Thompson in U. S. A. have been recorded.

Number of soils in each group	Total phosphorus, part per million part of soil	Total nitrogen
2	800—999	0·375
25	600—799	0·325
17	400—599	0·226
4	200—399	0·151
2	0—199	0·111

It will be of interest to record here that in general there is fair correlation between the nitrogen status and calcium phosphate status of some surface soils in the districts of Burdwan and Hoogly in West Bengal. (vide S. K. Mukerji, Government Publication on Manurial, Varietal and Agronomic Trials of crops in W. Bengal, 1956). This will be evident from the following table :—

BURDWAN							
Nature of soil	Latterite	Red soil	Damodar riverine land	Damodar flat land	Damodar up land	Ganga riverine land	Ganga flat land
% of CaO	0·16	0·11	0·322	0·31	0·23	0·81	0·38
% of P <sub>2</sub> O <sub>5</sub>	0·021	0·017	0·05	0·019	0·033	0·109	0·1
% N	0·05	0·022	0·046	0·032	0·048	0·074	0·075
pH	5·58	6·6	6·52	5·82	5·78	7·0	6·56

## HOOGHLY

	Ganga flat land	Ganga low land	Inundated Damodar riverine land	Damodar riverine
% CaO	0.4	0.84	0.21	0.16
% P <sub>2</sub> O <sub>5</sub>	0.04	0.10	0.07	0.063
% N	0.07	0.08	0.034	0.062
pH	5.74	6.8	6.8	5.0

The foregoing results show that the ratio of N/P of the above soils collected from Burdwan and Hoogly of which the average temperature is 27° varies from 5.4 to 1 the average being 2.7. As these soils are poor in lime, utilization of basic slag obtained from Kulti and other factories is bound to be profitable. In a rich soil at Allahabad, in front of the Sheila Dhar Institute of Soil Science, the total nitrogen is 0.25% and total P<sub>2</sub>O<sub>5</sub> is 0.4%. In this case the ratio of N to P is 0.62.

In soils, collected from the tea states of Assam, India, the N/P ratio varies from 0.56 to 2.9, average being 1.6. The N/P ratio of some Ceylon tea soils from planes varied from 1.84 to 2.38. In Nilgiris, in Madras, this ratio is 1.5, whilst the same value was obtained in Travancore. In Madhya Pradesh, the soils analysed are very poor in phosphorus and hence the values of N to P were very high. In Ceylon, some soils are collected from tea states at 2000 feet above sea level and in these soils, the N/P ratio varies from 1.8 to 10.3 with an average of 4.3. In Sumatra, the phosphate status is very low and in many fields, the surface soil shows a N/P ratio very large.

On the other hand, in the publications of the University of Alberta in Canada in their bulletins No. 21, 31, 32, 36, 42, 48, 51 & 53, numerous results of soil analysis have been recorded. From a survey of these results, it appears, that the N/P ratio of over 100 soil samples varies from 60 to 1.4. The average is 4.4 with 109 soil samples. It seems that on an average, the N/P ratio of soils of cold and temperate climates is appreciably higher than the same ratio obtained in tropical soils.

In a recent paper R. Dabin (International Soil Science Congress Paris 1956) has reported that in soils of Togo and Dahomey (Africa) there is a fair correlation between the total nitrogen and total phosphate and the values of N/P vary from 1.5 to 4.

A Kaila has reported that in Finnish cultivated mineral soils the ratio  $\frac{\text{Organic Carbon}}{\text{Organic phosphorus}}$  was found to vary from 100 to 150 and 40% of the total phosphorus in such soils is in the organic form. He has stated that the adsorption of nucleic acids by clay minerals and the formation of insoluble and aluminium compounds of phytin may be the cause of the slow mineralization of organic phosphorus compounds in these soils.

On the other hand, the mineralization in our soils, which are much warmer than the Finnish soils is quicker and the organic phosphorus is of the order of 5 to 10% of the total.

## NITROGEN FIXATION IN FIELDS WITH MANURE AND PHOSPHATE

In this connection it will be of interest to record the following results obtained by P. E. Karrer in U. S. A. in 1951

Average of 3 Fields :— TREATMENT		Nitrogen in Soil per acre in lb.		Corn yield in bushels.
No manure	...	1600	...	17
Manure	...	1760	...	36
Manure + Limestone	...	1830	...	38
Manure + Phosphate	...	1990	...	51
Manure + Limestone + Phosphate		2050	...	55

These results clearly show that the nitrogen content of a soil markedly improves when manure is mixed with phosphate proving a fixation of atmospheric nitrogen in this way.

It is generally acknowledged that the simple grass-legume ley is too low in minerals and that in consequence the health and specially the reproduction faculties of cattle and sheep are reduced. Hence, many farmers have adopted the practice of phosphating the stubble and, although, this gives good results, earlier application of phosphates causes a much better take of grass. There is no doubt that grass, when ploughed in with basic slag or finely divided soft phosphate rock, gradually undergoes oxidation and fixation of atmospheric nitrogen takes place. Moreover, in this system the phosphate is made available to the grass or legumes which flourish well specially in presence of phosphates. There is no doubt that both—dung and grass—when incorporated in the soil specially in presence of finely divided rock phosphate or basic slag, the carbonaceous substances present in the dung or the grass undergo slow oxidation with liberation of energy which is utilized in nitrogen fixation. In presence of phosphates this is accentuated. But if superphosphate is used, as is done in many countries, the velocity of oxidation of the organic matter in the soil is not as high as with basic slag or powdered phosphate rocks which are more alkaline than superphosphate. We have frequently observed that all oxidation processes by air are accelerated by alkali and retarded by acids. Hence, in temperate countries where the soil temperature is low and oxidation processes are slow, finely divided phosphate rock or basic slag after an interval of 4-6 months should produce better results in improving land fertility than superphosphate.

H. Greene (5th International Soil Science Congress 1954, Vol. I, page 154) has reported as follows:—"In Southern Rhodesia yields of maize are much increased when it follows a green manure such as sunnhemp (*Crotalaria juncea*) or velvet bean (*Mucuna* sp.) Animal manure has a valuable and lasting effect but response to nitrogenous and phosphatic fertilizers has been disappointing. At the Salisbury experimental station application of rock phosphate to the green manure has proved rather better than direct application of superphosphate to maize."

# FIXATION OF NITROGEN BY WATER HYACINTH (EICHHORNIA)

It is well known that water hyacinth is a great menace in different parts of this country, but, we have utilized this material in fixing atmospheric nitrogen when mixed with soil and it undergoes slow oxidation in air. The following results show clearly that there is marked fixation of nitrogen when the carbonaceous compounds present in water hyacinth undergo slow oxidation in soil and the nitrogen fixation is increased by light absorption as well as in presence of phosphates:—

Analysis of Water Hyacinth			Soil Analysis		
Loss on ignition	...	68.68%	C	...	0.239%
Ash	...	31.32%	N	...	0.0436%
Silica	...	11.215%			
Sesquioxide	...	8.9875%			
Fe <sub>2</sub> O <sub>3</sub>	...	1.45%			
CaO	...	2.858%			
MgO	...	0.9958			
K <sub>2</sub> O	...	5.32%			
P <sub>2</sub> O <sub>5</sub>	...	0.6759%			
C	...	41.91%			
N	...	2.387%			

## Soil + Water Hyacinth (1.5% carbon).

Period of exposure		Total carbon %	Total nitrogen %	Efficiency, i. e. mgm. of nitrogen fixed per gm. of carbon oxidized
LIGHT	...	0	1.7304	0.1272
	...	60	1.1308	0.1424
DARK	...	0	1.7304	0.1272
	...	60	1.3846	0.1335

## Soil + 0.5% P<sub>2</sub>O<sub>5</sub> as Tata Basic slag + 1.5% C as Water Hyacinth.

LIGHT	...	0	1.7154	0.1244	...
	...	60	0.7984	0.1552	33.5
DARK	...	0	1.7154	0.1244	...
	...	60	0.9226	0.1419	22.1

Our experimental results show that like dung, water hyacinth (Eichhornia) which is rich in nitrogen and potash, not only supplies the plant food materials it contains when ploughed in the soil, but, it also fixes atmospheric nitrogen copiously both in light and dark, specially in presence of phosphates. Consequently, 20 tons of water hyacinth mixed with 50 to 100 lbs. of P<sub>2</sub>O<sub>5</sub> in the form of basic slag, should prove to be an excellent manure in tropical soils and obtaining a compost rich in plant food.

It is interesting to note that the C/N ratio of fresh water hyacinth is 18 whilst that of cowdung is usually 20. Hence this material, which is largely available in U. P., Bengal, Orissa and Behar should be mixed with basic slag or bone and utilised in humus increase and conservation of soils.

#### LIGHT ABSORPTION INCREASES NITROGEN FIXATION

In our experiments carried on for 25 years, we have observed that in presence of sunlight or artificial light, the nitrogen fixation obtained by incorporating all kinds of organic substances in soil and allowing them to undergo oxidation in air is greatly enhanced by light absorption. Hence the amount of nitrogen fixed in mgms. per gm. of carbon oxidised i.e. the efficiency of nitrogen fixation, is always greater in light than in the dark, because the absorbed light is actually utilised in fixing nitrogen in the soil, both in presence or absence of phosphates. In this process, light energy is actually utilized in land fertility increase. Our results and conclusions have been fully confirmed by G. Bjälve of Sweden. The results recorded in this paper show clearly that the efficiency of nitrogen fixation in presence of light is always greater than in the dark, showing improvement of land fertility by light absorption.

It is well known that today the caloric intake of the best fed country of the world, i.e., Ireland is 3400 K. Cal. per day per capita. Whilst in India, which is the most ill nourished country in the world today is only 1600 K. Cal. Consequently the average caloric consumption per capita per day in the whole world can be considered to be 2500 K. Cal.

Assuming that 1200 kilograms of wheat and straw are produced per acre per year, the amount of energy available per acre is approximately 4800000 K. Cal from the wheat and the straw. On the otherhand it has been estimated that 500 K. Cal of solar energy fall on a square foot of land surface per day. This is equivalent to nearly 22 million K. Cal per acre per day. Hence the solar energy falling per acre per year is  $365 \times 22$  million K. Cal. Hence, the amount of energy actually utilized in the production of wheat and straw per acre is approximately 0.06% of the solar energy falling on an acre. This is certainly a very wasteful process.

In many of our experiments on nitrogen fixation in light, 100 mgms. of nitrogen are fixed per gm. of carbon oxidized and 50 mgms. in the dark.

Hence when  $2\frac{1}{2}$  tons of straw are added per acre of our soil and if the greater part of the carbon is oxidized with liberation of energy, the amount of nitrogen fixed per acre in light is approximately 1120 Kgms. in dark it is 560 Kgms. It is well known that 10 K. Cals are generated per gm. of carbon oxidized. Hence the amount of energy liberated by the oxidation of carbon in the  $2\frac{1}{2}$  tons of straw is equal to 112 million K. Calories. This amount of energy can fix 560 kgms. of nitrogen per acre in soil. Hence for fixing 1 kgm. of nitrogen by the absorption of chemical energy obtained from the oxidation of carbon of the straw 200000 K. Cal are needed. On the other hand in our experiments, 50 mgms of extra nitrogen are fixed by absorption of solar energy. Hence per acre of land, 560 kgms. of nitrogen are fixed by absorption of solar energy per year. It has already been stated that the solar energy falling per year per acre is  $365 \times 22$  million K. Cal. Hence for fixing 1 kgm of nitrogen by absorption of solar energy 1434000 K. Cal. are necessary. This is 7 times greater than the chemical energy needed for fixing the same amount of nitrogen,

It appears therefore in fixing atmospheric nitrogen in this process, the chemical energy of oxidation is utilized more efficiently than the sunlight which falls on the land. Hence, plant photosynthesis and nitrogen fixation aided by light absorption utilize solar energy in a very inefficient manner.

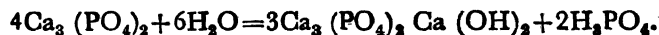
#### PHOSPHATES CHECK LOSS OF LIME AND MAINTAIN SOIL FERTILITY

We have discovered that the addition of phosphates to soils checks the loss of lime markedly by leaching with rain water and thus avoids the formation of acidic soils. This happens because in all soils  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is formed from tricalcium phosphate more readily than calcium bicarbonate by the action of carbonic acid on the calcium carbonate of soils. The dicalcium phosphate is much less soluble than calcium bicarbonate.

It has been observed that ordinarily the soil solution is poor in phosphate due to the sparing solubility of tricalcium, ferric, aluminium and perhaps titanium phosphates which are normally present in soils. Hence, a renewal of the amounts of phosphate in the soil solution is absolutely necessary for crop production. This is possible by increasing the calcium phosphate status of the soils all over the world by adding large doses of powdered soft phosphate rock or basic slag which is still inexpensive. It is well known that calcium phosphate or basic slag added to leys causes a greater growth of legumes and increased protein contents and enriches the land; but there is no doubt that even grasses without legumes lead to considerable soil improvement by fixing atmospheric nitrogen and preserving soil nitrogen, specially in the presence of phosphates. Hence, adding dung or growing grass leads to land improvement (Compare W. Davies, *The Grass Crop*, 1952, pp. 7, 256).

Our experiments clearly show that precipitated tricalcium phosphate, when shaken with water, yields more  $\text{P}_2\text{O}_5$  in the solution than the anhydrous dicalcium phosphate. Moreover, the natural phosphate rocks, when shaken with water, yield a fair amount of  $\text{P}_2\text{O}_5$  per acre.

It is well known that tricalcium phosphate in contact with water is copiously hydrolysed into free phosphoric acid and basic phosphate as in the following equation :—



This hydrolysis is checked in the presence of calcium carbonate or lime. Hence, the amount of phosphate existing in solution from basic slag has been found to be less than that from tricalcium phosphate, because, basic slag is rich in lime. It has been observed that carbonic acid converts tricalcium phosphate to dicalcium phosphate and small amounts of monocalcium phosphate. Hence, when phosphate rock or basic slag is mixed with organic matter undergoing oxidation in the soil due to the production of carbonic acid, dicalcium phosphate and a very small amount of monocalcium phosphate is formed and, thus, the availability of phosphate increases. Hence, manuring with organic matter mixed with phosphate rock or basic slag not only supplies nitrogen and available phosphate but also potash is made available to crops from the organic matter.

It appears, therefore, that organic manuring is not suitable in soils rich in ferric, aluminium or titanium phosphates. These compounds have to be partially converted into calcium and magnesium phosphates by the action of limestone or dolomite or free lime or basic slag before organic manuring can be profitable. Experiments show that the recovery of superphosphate increases from 27 to 41.7% on

liming of acid soils. Hence, in soils where large quantities of iron, aluminium or titanium phosphates are formed by adding superphosphate, as in acidic soils of Europe or America, organic manuring may be of little value and that is why people of Western Europe, where the soils are acidic and to which large quantities of superphosphate are added, have not yet appreciated organic manuring much. In tropical countries, however, where the soils are on the alkaline side and the phosphates present therein are chiefly calcium and magnesium phosphates, organic manuring with dung, straw, leaves, grasses, legumes, peat, lignite and even sawdust mixed with large doses of calcium phosphate or basic slag, is extremely profitable; because, the mixture is conducive to maintenance of soil neutrality and increase of humus the loss of which from soils causes infertility, alkalinity, increase of soil erosion and formation of desert conditions of land.

### VALUE OF ORGANIC MATTER IN CROP PRODUCTION

John B. Abbot of Vermont, U. S. A., has stated as follows: "If all accumulated soil wisdom of a hundred generations of master farmers were boiled down to just three sentences, one of these sentences certainly would be: provide for regular and frequent replenishment of the supply of organic matter in the soil"!

Similar observations have been recorded by Collings:—

"Nearly all soils are benefitted by the additions of suitable organic matter, no matter how much they may contain. It is a well-known fact that soils high in organic matter contain more phosphorus readily available to plants than do soils low in organic matter."

"Struthers and Seiling in 1950 found that organic anions, such as citrate, are nature's effective agents for preventing phosphate fixation by iron and aluminium in neutral and acid soils, and for making available the phosphorus that has already been fixed. Jensen in 1917 found that the addition of organic matter to a soil increased the solubility of both calcium and phosphorus 30 to 100 per cent."

Moreover, the following experiments on potatoes carried out at Rothamsted for a number of years in which a given dressing of straw and nitrogen was ploughed into the soil, are compared with the same quantity of straw rotted with the same quantity of nitrogen in a compost heap and then applied to the land. The ploughed-in straw has always a better yield than the compost as shown below:—

12 years (1934-45).

	Year of applying straw.		Year after application.	
	Compost.	Straw ploughed-in.	Compost.	Straw ploughed-in.
Potatoes (tons per acre)	7.86	9.40	7.40	7.97
Sugarbeet, sugar (cwt. per acre)	37.0	41.2	36.4	38.2
Barley, grain (cwt. per acre)	27.7	31.2	26.5	27.9

The above experimental results obtained at the famous Research Station of Rothamsted are strong support of the conclusion drawn in 1935 by me from our experiments that a mixture of ammonium sulphate and organic matter is a better fertilizer than ammonium sulphate alone.



Collings has stated (COMMERCIAL FERTILIZERS, 1947, page 436) :—

"Many agricultural experiment stations have shown that the incorporation of green manures in the soil, in addition to a complete fertilizer, results in an increase in the yields of succeeding crops. Most soils are benefitted by the addition of suitable organic matter regardless of the quantity they contain. Johnson (1924) at the Virginia Truck Experimental Station, found that when one ton of a 6-4-8 fertilizer was applied, the average yield of potatoes was 155 bushels, but when a green manure crop was turned under previous to the addition of the fertilizer, the average yield was raised to 232 bushels." Again, on page 213, it has been stated : "When virgin soil is put under cultivation, a rapid decay and nitrification of the organic matter is induced, and, the resulting carbonic and nitric acids materially aid in making available the insoluble phosphates of the soil. As supply of organic matter decreases so do the quantities of carbonic and nitric acid and in turn the quantity of available phosphoric acid. This natural process has played in an important role in increasing the demand for superphosphates as well as for the potashes in the older populated areas."

F. E. Bear and B. L. Prince (New Jersey Agricultural Experiment Station Bulletin No. 757, June 1951) have reported as follows :—

"When crop residues were returned to the soil, the yield increase in terms of total produce of snap beans and carrots averaged 12%. A rye cover crop added 7½%, and 2¼ tons of cornstalks another 14%. Thus, for organic matter additions totalling a little more than 5 tons an acre a year, the yield increase was 33½%."

"The best organic matter system under continuous culture raised crop yields to 39%. This involved crop residues cover crops and soy beans for mulching every second year. The best 5-crop rotation programs raised average yields more than 60%. These involved letting the land grow up to weeds, using winter grains and deep-rooted legumes, growing sweet corns and soy beans or employing similar procedure two years out of every four."

In a recent paper, I. V. Tuirin (Intern. Soil Science Congress, Paris, 1956) has emphasised on the value of legumes and dung in the maintenance of the nitrogen status of land in U. S. S. R.

Similarly, in Europe, the value of organic matter in soil fertility has been emphasized by A. Demolon and H. Burgevin working in France for a number of years, and, beneficial results are obtained by ploughing-in straw. Similarly, O. Flieg, working in Germany, reported on the value of straw in land fertility. In Russia also, M. V. Fedorov found straw beneficial. In England Thornton reported that soy beans, horse beans are benefitted by straw cut into pieces. In our researches on the problem of nitrogen fixation by adding organic matter to soil, we have, for the first time, explained satisfactorily that the chief role of organic matter in improving land fertility is its power to fix atmospheric nitrogen and preserving nitrogen of the soil. Moreover, the value of organic matter as a soil improver is greatly enhanced by calcium phosphates, and, this mixture must be utilized all over the world in permanent agriculture.

#### FAMOUS CLIFTON PARK AND COCKLE PARK EXPERIMENTS

It is well known that Elliot in his farming system at Clifton Park, England insisted on the ploughing of land and the maintenance of soil fertility. His achieve-

ment was to show by his crops that ploughing and soil fertility are interdependent and the ley, which is a product of the plough, keeps up the soil fertility.

On the other hand, at Cockle Park, in Northumberland, excellent results were obtained by Somerville and others in their "manuring-for-mutton" experiments by using initially 10 cwt. of basic slag containing 200 lbs. of  $P_2O_5$  per acre. In this system, the beneficial result is attributed chiefly to the increased growth of wild white clover. In Elliot's system, a good leguminous crop like late-flowering red clover, alsike clover, kidney vetch, ordinary white clover, lucerne etc. formed the base of his manuring. Moreover, he insisted on the beneficial effect of the use of deep-rooted plants. Elliot never emphasised on the importance of phosphates in his system. But, there is no doubt that his deep-rooted plants played an important part in subsoiling and making phosphates available from deeper layers of the land.

It will be interesting to record that from the total nitrogen point of view the land in Clifton Park was better than that at Rothamsted. The original total nitrogen in Cheviot Turf was 0.336%. In another field in Clifton Park the total nitrogen was as follows :—

	1902	1903	1904	1905	1906	1907
Nitrogen %	0.263	0.300	0.285	0.236	0.281	0.288

At Rothamsted, the soil originally contained probably 0.12% total nitrogen when the experiments started in 1844. The following results were obtained in 1914 by manuring every year with inorganic nitrogenous compounds or dung and wheat was grown every year :—

	Ammonium sulphate				Sodium nitrate		Farmyard manure.
Nitrogen added per acre in lb.	None	43	86	129	43	86	200
Nitrogen in soil in 1914 %	0.104	0.111	0.119	0.129	0.116	0.115	0.236

The foregoing Rothamsted results show that in the field receiving farmyard manure, considerable improvement in the nitrogen status of the soil has taken place, whilst with inorganic fertilizers there has been an appreciable deterioration.

It is well known that the available nitrogen in temperate country soils does not exceed 2%, whilst in tropical soils, the available nitrogen may be 10 to 30% of the total nitrogen. Due to leaching of lime, most of the temperate country soils are acidic and in these soils, the oxidation processes causing the formation of available nitrate are slow. These oxidation processes are activated by ploughing as insisted upon by Elliot or by adding basic slag as at Cockle Park. The basic slag not only supplies phosphates to crops but also lime, manganese and vanadium compounds which help oxidation in the soil and produces ammonium salts and nitrates from the proteins and other nitrogenous compounds present in the soil. Moreover the slag causes the fixation of atmospheric nitrogen by the oxidation of the soil humus and hence the C/N rates of the soils is decreased.

In South Africa in the Orange Free State, Moroccan rock phosphate compared well with superphosphate. In Natal, Egyptian rock phosphate was found to be as effective as superphosphate in maize.

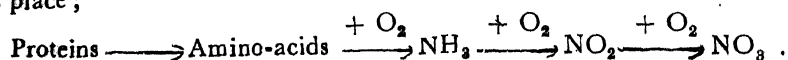
It is generally believed in Europe that under ordinary conditions of cultivation legumes can only lead to improvement of the nitrogen status of the soil; but, a plot of land in the Geescroft Field, Rothamsted, covered with grass without any leguminous plants, showed an increase in nitrogen from 0.105 to 0.145% in 20 years, i.e., 44 lbs. of nitrogen increased per year per acre. Similarly, Lyon and Buckman at Ithaca and White, Holben & Richer in Pennsylvania have reported that soils under grass ley free from legumes and *Azotobacter* gained considerable amounts of nitrogen every year. All these observations can be satisfactorily explained from our experiments on the fixation of atmospheric nitrogen in soils on the addition of organic substances like molasses, dung, straw, grass, leaves, peat, lignite etc. We have concluded that these compounds not only supply plants nutrients they contain and add colloidal substances to the soil, improve the tilth and crumb formation and water retention capacity of the soil as hitherto believed, but, they also undergo slow oxidation in the soil and liberate energy which is utilized in fixing atmospheric nitrogen and enrich the soil from the nitrogen point of view. Moreover, the carbonaceous non-nitrogenous compounds present in the soil or added to it preserve the nitrogenous materials of the soil or the added nitrogenous compounds just as carbohydrates act as protein spacers in the animal body because they behave as negative catalysts in the oxidation of proteins. From extensive experiments we have come to the conclusion that the fixation of atmospheric nitrogen by the addition of organic matter to soil is greatly enhanced by the presence of calcium phosphate as well as by light absorption. Also, we have observed experimentally that soils rich in calcium phosphate when ploughed undergo slow oxidation in contact with air and can fix atmospheric nitrogen by the oxidation of carbonaceous materials present in the soil humus. Moreover, when calcium phosphate is added to soils, not rich in calcium phosphate, fixation of atmospheric nitrogen takes place even in the absence of added organic matter.

From our recent experiments we have come to the conclusion that the leaching of lime from soils is considerably decreased by the addition of phosphates. Calcium phosphate, which is less alkaline than calcium carbonate when added to soils, does not destroy soil humus as rapidly as calcium carbonate does by oxidation.

Land under grass, free from legumes, becomes richer in nitrogen chiefly due to the fixation of atmospheric nitrogen from the oxidation of the organic matter incorporated in the soil from the grass and preserving the soil nitrogen from rapid nitrification and loss and improving the physical properties of the soil. Calcium carbonate and specially calcium phosphate are beneficial to this process. It has already been stated that when dung is added to soil, the nitrogen status considerably improves. It appears that dung added to soils performs the same part as the growing of grass by fixing atmospheric nitrogen slowly, preserving the soil nitrogen and improving the physical properties of the soil. It is well known that calcium phosphate or basic slag added to leys causes a greater growth of legumes and enriches the land, but, there is no doubt that even grasses without legumes lead to considerably soil improvement on the application of powdered soft phosphate rock or basic slag by increased nitrogen fixation as observed by us. Hence, adding dung or growing grass aided by calcium phosphates improves the land considerably. Like dung, the C/N ratio of grasses is usually greater than

the C/N ratio of legumes which are naturally richer in nitrogen than grasses. Hence, like dung, the residual effect of grasses as manure is greater than that of legumes. Consequently, a mixture of grasses and legumes in leys improves soil fertility better than either grasses or legumes singly. The greater amounts of carbonaceous compounds present in grasses may, under favourable conditions, fix atmospheric nitrogen in the soil markedly and can act as protectors of the nitrogenous compounds present in legumes or soils from undergoing rapid nitrification and loss.

Dhar and co-workers have proved that when nitrogenous fertilizers or proteins are added to the soil under aerobic conditions, the following changes takes place ;



It is known that these changes are oxidation reactions which lead to the production of available nitrogen in the soil, are accelerated and favoured by increased aeration, high temperature and absorption of light. In these processes the unstable substance, ammonium nitrite, is formed and can readily decompose as in the following equation specially in presence of light or in acid soils :



Thus, a mixture of grass and legumes behaves like a mixture of dung and ammonium sulphate or a mixture of straw and ammonium sulphate, the mixture being more profitable in crop production than either dung or grass or straw or ammonium sulphate or legume acting alone. It has been stated that the nitrogen in dung is less readily available than that in legumes. This is due to the fact that the C/N ratio of dung is usually higher than that of legumes and, hence, the nitrification of the proteins and other nitrogenous compounds present in the dung is slower than that of the nitrogenous compound present in legumes. The greater amounts of carbonaceous compounds present in dung or grasses retard the nitrification of the proteins in dung or grass to a greater extent than that taking place in legumes. But, in course of time, the carbonaceous substances in dung or grass undergo oxidation and, hence, the retarding effect on nitrification of the nitrogenous compounds present in dung or grass decreases and, thus, the nitrogenous compounds in dung or grass and those fixed from the air undergo nitrification and become available to crops.

It is well known that ploughing increases aeration in a soil and, hence, the ploughing insisted upon by Elliot for maintaining soil fertility is helpful in fixing nitrogen by oxidation of the organic matter of the grass and legumes and also in the liberation of available nitrogen by enhanced oxidation of the proteins present in the soil or obtained by fixation of atmospheric nitrogen.

Recently, Dhar and co-workers have obtained appreciable nitrogen fixation when the whole of the leguminous plants like sunhemp (*Crotalaria Juncea*) or lucerne or clover is ploughed in the soil and allowed to undergo slow oxidation, and, this nitrogen fixation is greatly enhanced by adding calcium phosphate and by light absorption. Moreover, their experiments clearly show that the availability of calcium phosphate or basic slag is considerably increased in the presence of organic matter undergoing slow oxidation due to the formation of dicalcium and small amounts of mono-calcium phosphates from the tricalcium phosphate present in phosphate rock or basic slag and carbonic acid produced from organic matter. Hence, it appears that for improving the humus status or land fertility, as insisted upon by Elliot, ploughing in of grasses aided by calcium phosphates performs the

same function as the ploughing in of dung and calcium phosphate. Consequently, grasses, incorporated in the soil by ploughing, can behave as dung and the dung cart is not indispensable in the maintenance of soil humus and fertility because grasses and calcium phosphate can supply nitrogen, potash and available phosphate and decrease the leaching of lime. It appears, therefore, that a mixture of organic matter and calcium phosphate or basic slag, when ploughed in the soil, can serve as an excellent fertilizer for crop production after an interval of 4 to 7 months required in the partial breaking down of the organic substances ploughed in lands in the cold countries. Consequently, our experimental observations on the fixation of atmospheric nitrogen by adding organic matter and phosphates can explain satisfactorily the practical achievements of Elliot at Clifton Park and of Somerville and others at Cockle Park, and, a combination of these two classical systems leads to greater fertility and can avoid the use of artificial nitrogenous fertilizers by fixing atmospheric nitrogen and production of more available nitrogen, potash and phosphates. We are convinced from our experimentals lasting for over 25 years that grasses, straw or dung, when ploughed in the soil along with calcium phosphates, fix atmospheric nitrogen all over the world and can perform the same function in land improvement as the growing of legumes. The time interval between the ploughing in of the organic matter and the sowing of a crop has to be longer in temperate country soils than in tropical soils.

Land fertility depends a good deal on its calcium phosphate status, because, land rich in calcium phosphate can readily fix atmospheric nitrogen by the oxidation of organic matter which is naturally present and can maintain its neutrality by avoiding leaching of lime. That it is desirable to increase the calcium phosphate reserve of the soils by adding cheap phosphatic materials like basic slag and powdered soft phosphate rock is shown by the classical Cockle Park experiments lasting for over 50 years where a dressing of 10 cwt. of Thomas slag per acre was found better than two dressings of 5 cwt. each. Recently, K. G. Baker and E. L. Mayton have observed that heavier and less frequent applications of superphosphate produce better yields of pastures than frequent applications of smaller amounts of superphosphate. In recent years it has been reported from various parts of U. S. A. that fresh rather than composted manure reinforced with 30 to 50 lbs. of superphosphate per ton of manure applied to the soil produced good results in pastures. Moreover, the Cockle Park experiments demonstrate that basic slag in combination with dung is highly satisfactory for old land hay; and dung is of greater value than artificials for the light soils, and, there is increase of total nitrogen in soils treated with phosphates. Moreover, C. G. Hopkins, J. G. Mosier, E. Van Alstine and F. W. Garrett have reported a marked beneficial effect of a mixture of plant residues and rock phosphates in crop production. Also, Lars Eredriksson working with the organic Gytta soils of Sweden observed that basic slag is very good for such soils.

In our recent experiments on composting of dung or wheat straw, or water hyacinth by the addition of small amounts of soil, the incorporation of powdered phosphate rock or basic slag or a mixture of powdered phosphate rock and superphosphate has been found to be highly beneficial by fixing atmospheric nitrogen in these composts. It is well known that in composting of plant materials there is usually a loss of nitrogen. Hence, there is very strong experimental evidence in favour of the view that the calcium phosphate reserve of soils must be improved for permanent agriculture and there is very good correlation between the total phosphate and total nitrogen of soils. Sir John Russell is right in his statement that the "phosphate supplies may yet become the factor that will determine the course of history".

## A NEW METHOD OF SOIL CONSERVATION AND IMPROVEMENT BY UTILISATION OF CHEMICAL AND SOLAR ENERGY

Great thinkers like H. Bergson, A. Einstein and others became highly concerned about the problem of world soil conservation and maintenance and improvement of land fertility. From our researches we are convinced that fertile lands have been formed from the geological rocks by the fixation of atmospheric nitrogen aided by sunlight and increase of soil humus by the incorporation and partial oxidation of organic substances created by plants in photosynthesis by solar light and calcium phosphates. This mixture is easily the best method of soil conservation, increase of soil humus and fertility and increased crop production to cope with the rapid augmentation of world population. Man has utilized and frequently wasted the fertility of land created by the leaves of forest trees and growing grasses. We have observed that in breaking new land for cultivation, in the process of nitrification, greater amounts of proteins and other nitrogenous compounds in the soil are lost as nitrogen gas than the amounts taken up by crops. This can be rectified by ploughing in large amounts of organic matter enriched with calcium phosphate.

It is well known that when nomadic man with his animals first settled down and began agriculture, he used the dung of his animals for crop production. In the Greco-Roman period, the Legume Lupin seems to have been fairly extensively used in fertility improvement. Only during the last hundred years chemical fertilizers are being utilized by the industrially advanced nations in cultivation but the amounts used are still inadequate. In the East, where the majority of human beings of the world subsist, artificial fertilizers are practically unknown. Even before the last European war the amounts of artificial nitrogen used per acre in pounds were small as is evident from the following table:—

Belgium (28.5), Holland (24.8), Germany (15.6), Denmark (10.3), Norway (6.0), Sweden (5.24), Italy (4.3), France (4.0), Great Britain (2.5), U.S.A. (1.36), Poland (0.73) and Hungary (0.15).

At present larger doses of nitrogen are being utilised in many countries.

The efficiency of the industrial methods of fixing nitrogen being very low, the cost of production of fixed nitrogen has remained high and this is the chief reason why the amount of nitrogen added in crop production has remained low. It is no wonder, therefore, that only 3% of the world food production has been attributed to artificial nitrogenous fertilizers in the British Association Meeting of 1948 presided over by Sir John Russell and reported in NATURE (Vol. 164, No. 4171, page 597) as follows:—

“At present only 3% of the world food production can be attributed to the use of nitrogenous fertilizers. To raise the food by 10%, that is to say one hundred million tons, involves a fourfold increase in supplies of fixed nitrogen at an approximate capital cost of £ 1,50,00,00,000. This would take a minimum of 15 years to achieve.”

Thus soil humus nitrogen, including 5 million tons of nitrogen believed to be fixed by legumes, is the chief nitrogen source of the world food production. There is no doubt that for producing 1000 million tons of food materials harvested in the whole world no less than 100 million tons of fixed nitrogen are needed.

We have developed a cheap and easily workable method of land improvement based on the fixation of atmospheric nitrogen by decaying organic matter aided by phosphates. Our method of fixing atmospheric nitrogen by organic matter and phosphates is much more efficient than the industrial method and is as effective as that by legumes. We are convinced from our experiments that a mixture of phosphates and organic matter is extremely useful for permanent agriculture as this mixture fixes atmospheric nitrogen copiously and supplies available nitrogen, phosphate, potash and trace elements. Moreover, from a large number of experiments we have come to the conclusion that calcium phosphate markedly decreases the washing away of lime from soils. Hence, it appears that phosphatic fertilizers should always be reinforced by organic matter. Our conclusion is that the mixture of organic substances like farmyard manure, water hyacinth, straw, leaves, peat, lignite, grass and calcium phosphate, when added to soils, can build up soil fertility permanently by decreasing acidity and fixing atmospheric nitrogen and supplying available N, P, K and trace elements and decreasing the leaching of lime. Hence, it is highly desirable to increase the calcium phosphate status of land all over the world in permanent agriculture by utilising cheap phosphatic fertilizers such as basic slag, soft phosphate rocks etc. We are carrying on a large number of experiments in the laboratory as also field trials with Indian basic slag, phosphate rocks and superphosphate prepared from these phosphate rocks. In our country, the Tata Steel Works are producing 1 million tons of basic slag per year which has not found any use so far. Moreover, we are studying the decomposition of all types of phosphates by water, carbonic acid and weak organic acids. Also, we are testing systematically the various methods of determining the available phosphate in soils. Our method of improving land fertility at a small cost, which is a realistic and simple programme readily applicable in tropical and temperate climates, is as follows :—

Straw (of wheat, barley or oat) at  $2\frac{1}{2}$  tons per acre mixed with 50 to 100 lbs. of  $P_2O_5$  in the form of basic slag (Thomas slag) or finely-divided soft phosphate rock is ploughed in August or early September when the fields are available after harvesting of crops. In this process organic substances present in straw undergo slow oxidation with liberation of energy and nitrogen of air is fixed on the soil surface and this is aided by absorption of sunlight falling on the soil. Moreover, the carbonic acid and other weak organic acids produced in the oxidation of the organic matter make the basic slag or the soft phosphate rock slowly available to the crops. The potash present in the straw is also available to plants in course of time. Hence, ploughing of straw or dung or grass or water hyacinth with basic slag or finely-divided soft phosphate rock can supply all the important ingredients needed for crops.

In Sweden increased yields of wheat and oat upto 25% by ploughing in straw as recommended by me have been obtained. A large number of field trials are being continued in Sweden with straw in presence of basic slag and soft phosphate rock and superphosphate, etc. without any nitrogenous fertilizers. Moreover, Herr G. Bjalfve of the Royal College of Agriculture, Uppsala—7, Sweden, has been able to obtain marked nitrogen fixation with straw or other energy materials mixed with sand or soil; and, that light increases nitrogen fixation has been definitely confirmed by Mr. Bjalfve in laboratory experiments.

Recently, we have developed a new and original method of reclaiming alkali lands by treating them with a mixture of organic matter and powdered phosphate rock or basic slag. We believe that this method is going to be very profitable in the reclamation of vast areas of alkali lands existing in this world. Hence,

16 research scholars who are carrying on research work for their Doctor's Degree are conducting intensive investigations on Indian basic slags, phosphate rocks, superphosphate, all the calcium phosphates and magnesium, iron aluminium and titanium phosphates from chemical, physical and microbial points of view.

In Allahabad the average temperature is  $26^{\circ}$  and at Uppsala where I worked for about a year in 1953-54 it was  $5^{\circ}$ . In Rothamsted it is about  $8^{\circ}$  and at Versailles it is  $9^{\circ}$ — $10^{\circ}$ . It is well known that oxidation processes are slowed down at low temperatures. But, I believe, that even at an average temperature of  $9^{\circ}$  or  $10^{\circ}$ , our method should be applicable.

In tropical soils the total nitrogen is of the order of 0.04% to 0.05%. In temperate country soils the nitrogen content is almost three times greater, i.e. of the order of 0.12% (as in Rothamsted) to 0.14% (as in some Swedish soils). In Rothamsted by adding farmyard manure at the rate of 14 tons containing 200 lbs. of total nitrogen per acre and growing wheat every year, the total nitrogen went up to 0.25% within a period of about 50 or 60 years. But on adding artificials containing 43, 86, 129 and even 200 lbs. of total nitrogen in the form of ammonium sulphate or sodium nitrate and suitable amounts of potash and superphosphate and growing wheat every year, there was a little fall of total nitrogen content in 50—60 years. Similar results have been recorded in U. S. A. and Denmark. In our experiments carried on by Dr. B. G. Chatterji using dung in 3 doses spread over 3 years, the total nitrogen rose upto 0.2% from 0.04% while using leaf in 3 doses the total nitrogen rose upto 0.11% from 0.04%. Hence, it is quite clear that organic matter alone can lead to increase of land fertility and improve the nitrogen status markedly.

The good soil in front of the Sheila Dhar Institute of Soil Science where municipal rubbish was dumped and where dead bodies were buried occasionally showed a nitrogen status of 0.25%. Similarly, the newly acquired land which was frequently under Ganges water, lying on the other side of the Lajpat Rai Road, was also dumped with municipal rubbish for a year and to which Tata basic slag was also added in small lumps. On analysing some samples of soils the following results were obtained :—

*Analysis of different samples of Farm Soil.*

		Total carbon %	Total nitrogen %	C/N ratio
1. No phosphate	...	1.90	0.172	11.0
2. Tata basic slag	...	1.766	0.331	5.3
3. Tata basic slag	...	2.01	0.270	7.4
4. Tata basic slag	...	1.89	0.279	6.7

It is clear, therefore, that on adding calcium phosphate either in the form of bones or basic slag containing 8 to 10%  $P_2O_5$ , the nitrogen status of land can be permanently improved and bumper crops can be obtained on such improved lands.

In Howard's method of composting of plant materials, the compost obtained usually contained approximately 1% total nitrogen. We have carried on a large number



of experiments in composting with water hyacinth, weeds, straw, dung etc. with or without finely-divided rock phosphate or bone or basic slag and we have observed that the total nitrogen of the phosphated compost is of the order of 1.8 to 2%, i.e. much richer than the average Howard compost. Hence, for the last 5 or 6 years we are preaching the gospel of land fertility improvement by a mixture of organic matter and finely-divided phosphate rock or basic slag or bone. Man has used organic matter or phosphate for land improvement separately. I am insisting, however, that the two together are more valuable in permanent agriculture than either organic matter or phosphate alone. Hence, dung or straw or legume in green manuring should always be incorporated with bone or powdered phosphate rock or basic slag or superphosphate. Similarly, in phosphating land better results are always obtained by adding organic matter along with phosphate. In Italy about 30 years ago, excellent results were obtained by adding superphosphate, but, now, due to exhaustion of organic matter, such beneficial results have not been obtained. Similar observations have been recorded in South Africa and Australia. In Uttar Pradesh (India) phosphates do not produce very good results but in Bengal phosphating is more profitable because Bengal soils are usually richer than Uttar Pradesh soils in organic matter. As organic matter is constantly added to soil by photosynthesis, land fertility can be readily improved at a small cost by adding cheap sources of phosphates like soft phosphate rock of Africa or basic slag. Hence, our researches have convinced us that the British Government have to be congratulated because of the subsidy granted to farmers for the use of basic slag since 1937. This shows that the English nation is capable of taking a practical important step in land fertility improvement as a permanent measure.

At Illinois, a mixture of organic matter and rock phosphate has been found very profitable.

Sir Charles Ellis, F. R. S., who was the Scientific Member of the British National Coal Board told me that a lot of coal slurry is available as a waste product of the coal industry. From our experiments carried on with finely-divided coal, lignite and peat mixed with basic slag or phosphate rock, we are convinced that there is appreciable nitrogen fixation and the availability of phosphate increases.

As coals, lignite, peat etc. are rich in aged humus they can be utilised as manures when mixed with basic slag or finely-divided rock phosphate which help in the oxidation processes in the system and make the nitrogen in coal, lignite or peat available to crops.

I am convinced that a judicious application of plant materials (formed in photosynthesis) mixed with cheap phosphatic sources like basic slag or finely-divided phosphate rock will lead to land fertility improvement and better crop production all over the world.

Also in composting all plant materials without nitrogen or potash, addition of calcium phosphate fixes atmospheric nitrogen and improves the quality of the compost.

#### LOSS OF SOIL HUMUS BY LARGE AMOUNTS OF MINERAL NITROGENOUS FERTILIZERS AND SOIL DETERIORATION ON CULTIVATION.

Sir John Russell has unequivocally stated in "50 Years of Field Experiments at Woburn" that both in Woburn and Rothamsted soil deterioration has been observed not only in continuous cropping but even in rotations when the land has been fertilised by ammonium sulphate or sodium nitrate and minerals.

The followers of land manuring by organic substances only claim that artificial fertilizers accelerate the breaking down of soil humus. G. Ruschmann holds the same view. On the other hand, E. M. Crowther, in his survey of the Woburn experiments, has stated that the effects of inorganic fertilizers on the losses of organic matter from the soil were insignificant. He has observed that in all Woburn permanent wheat and barley plots without farmyard manure the nitrogen contents fell from 0.16 to 0.10 per cent, i.e. about 1/3rd. of the soil nitrogen was lost from the surface soil in 50 years even when sodium nitrate or ammonium sulphate was added. The two plots with farmyard manure added at the rate of 105 lbs. of nitrogen per acre for 30 years and 82 lbs. nitrogen for 20 years just balanced the losses of nitrogen from the soil.

In many countries quantitative results are accumulating in favour of the view that addition of mineral nitrogen in fairly heavy doses accelerates the loss of the humus nitrogen as is evident in the observations in Rothamsted, Scotland and U. S. A.

Also, the Rothamsted results show definitely that the recovery of nitrogen is less than the amount added when ammonium sulphate is the fertilizer used because loss of nitrogen gas takes place in the process of nitrification of ammonium sulphate in the soil due to the formation of and decomposition of the unstable substance ammonium nitrite ( $\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O} + 718 \text{ k. Cal.}$ ), as emphasized by the workers in Allahabad, India.

It is evident from the results recorded in previous pages that when a heavy dose of sucrose is mixed with soil, there is considerable nitrogen fixation even in the absence of phosphates. The original nitrogen content of the soil is 0.043% but due to the fixation of nitrogen in the slow oxidation of sucrose, the nitrogen content of the system goes up to 0.0675, i.e. an increase of more than 50% of the total nitrogen in light. In the dark, the nitrogen increase is less and the total nitrogen goes up to 0.052%. As soon as phosphates are added, the nitrogen content shows an increase of 250% in light whilst in the dark the nitrogen increase is about 40 to 45% in presence of phosphates. These remarkable results conclusively prove that organic matter mixed with phosphates forms a very valuable source of land fertility improvement.

With dung, when a heavy dose is added, the mixture of soil and dung at the beginning shows a nitrogen content of 0.0942%. In absence of phosphates and in presence of light, the nitrogen content goes up to 0.108%, i.e. an increase of about 15%. In presence of Bihar rock phosphate the total nitrogen content of the mixture in light goes up to 0.1407% from 0.0934% showing an increase of about 50%. Similar results have been obtained with straw and water hyacinth.

In this process of increase of land fertility, the chemical energy liberated in the slow oxidation of the organic compounds and the solar light absorbed on the soil surface are actually utilized in fixing atmospheric nitrogen in the soil and this is a cheap method of soil improvement.

Consequently, we are convinced that a mixture of organic matter like straw or dung with basic slag which is being subsidized in England can be as effective in increasing land fertility as legumes. It is well known that approximately 50—100 lbs. per acre of nitrogen are ordinarily fixed by a good crop of legume in the West. In our experiments with dung and finely-divided phosphate rock or basic slag more than 100 lbs. of nitrogen can be fixed per acre. Our contention is that for enriching the soil from the nitrogen point of view, dung or straw plus phosphate is at

least as good as legume. The world experience is that a heavy dose of phosphate is good for crops and the soil because phosphate is not much leached by rain and hence always a residual effect of phosphate is observed.

We have established from our experiments that the leaching of lime is appreciably reduced by adding calcium phosphates which can maintain soil neutrality effectively.

#### RECLAMATION OF ALKALI LAND BY A MIXTURE OF ORGANIC MATTER AND CALCIUM PHOSPHATES

Recently, we have discovered that a mixture of SANAI (sann hemp) and phosphate rock or basic slag can permanently reclaim very bad alkali land. This is a very profitable and cheap method of reclaiming all alkali lands and depends on the following principle :—

The carbonic acid produced in the oxidation of SANAI (sann hemp) can readily convert calcium-tri-phosphate to the di-phosphate which can slowly supply calcium ions to the soil solution in small amounts and, thus, calcium carbonate is formed by the action of the alkali present in alkali soils and the calcium ions obtained from  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . We have also observed from our recent experiments that a mixture of organic matter and calcium carbonate is less profitable in reclaiming alkali soils than a mixture of organic matter and calcium phosphate, because,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is formed more readily by the action of carbonic acid on tri-calcium phosphate than the formation of calcium bicarbonate due to the action of carbonic acid on calcium carbonate. The dissociation constant of carbonic acid is larger than the 3rd. dissociation constant of phosphoric acid and that is why the formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is more easy than the formation of  $\text{Ca}(\text{HCO}_3)_2$ . Hence, in reclaiming alkali soils calcium phosphate is much better than calcium carbonate along with organic matter. Moreover, in the nitrification of proteins present in legumes (like SANAI and DHANCHHA) nitrous and nitric acids are formed which are profitable in the reclamation of alkali lands. Hence, our researches have thrown considerable light on the viewpoint that the world food production is limited by the phosphate reserves of soils which should be copiously increased.

Some of our recent observations are recorded in the following tables :—

##### *Percentage chemical composition of alkali soil used.*

Moisture	...	...	1.39
Loss on Ignition	...	...	2.50
HCl insoluble	...	...	84.51
Sesquioxide	...	...	7.05
$\text{Fe}_2\text{O}_3$	...	...	3.38
$\text{CaO}$	...	...	1.06
$\text{MgO}$	...	...	1.31
$\text{K}_2\text{O}$	...	...	1.10
$\text{P}_2\text{O}_5$	...	...	0.142
Available phosphate (2% citric acid)	...	...	0.0318
Ex — Ca	...	...	3.572 m. e.
Total carbon	...	...	1.135
Total nitrogen	...	...	0.0353
pH	...	...	10.00

*Analysis of Water Extract of the Soil*

		( % )
Total soluble salts	... ..	0.8960
Carbonate	... ..	0.1347
Bicarbonate	... ..	0.4376
Chloride	... ..	0.0302
Sulphate	... ..	0.0060

*Percentage composition of Sunn-hemp*

Total carbon	... ..	37.701
Total nitrogen	... ..	1.232
CaO	... ..	2.100
MgO	... ..	0.160
P <sub>2</sub> O <sub>5</sub>	... ..	1.518

ANALYSIS OF :—

ROCK PHOSPHATE

BASIC SLAG

P <sub>2</sub> O <sub>5</sub>	... ..	19.56	7.90
CaO	... ..	11.62	32.2
MgO	... ..	0.71	2.55
Carbonate	... ..	5.31	23.82

200 gms. Alkali soil + 26 gms. Sunn-hemp + 2% Basic slag

Period of exposure in days	Total carbon %	Total nitrogen %	Percent carbon oxidised	Ex-Ca in m.e. %	Available phosphate %	pH
0	4.5900	0.1600	...	3.572	0.0960	10.00
60	2.6170	0.1370	43.00	5.952	0.1295	9.50
120	2.2105	0.1252	53.00	7.810	0.1370	9.20
210	1.8108	0.1062	60.55	8.520	0.1410	8.60
365	1.7045	0.0968	62.86	8.645	0.1517	8.40

200 gms. Alkali soil + 26 gms. Sunn-hemp + 2% Bihar Rock Phosphate

0	4.5900	0.1600	...	3.572	0.0321	10.00
60	3.0642	0.1452	33.25	6.548	0.0678	9.40
120	2.7705	0.1360	39.00	8.627	0.0823	8.70
210	2.4704	0.1221	46.00	9.310	0.0871	7.90
365	2.1542	0.1115	53.07	9.510	0.0821	7.80

200 gms. Alkali soil + 26 gms. Sunn-hemp

0	4.5900	0.1600	...	3.572	0.0293	10.00
60	3.2462	0.1254	29.1	4.502	0.0434	9.70
120	3.0103	0.1145	34.1	5.324	0.0514	9.60
210	2.8004	0.0989	40.0	5.921	0.0573	9.20
365	2.5254	0.0927	45.0	6.457	0.0590	8.90

The foregoing results show clearly that in presence of rock phosphate, which is less alkaline than basic slag, Sunn-hemp can decrease the pH of a bad alkali soil considerably and improve the exchangeable calcium of the system. Even in presence of basic slag, the fall in pH and increase of exchangeable calcium is more pronounced than with Sunn-hemp alone.

In field trials in Soraon, near Allahabad bad alkali lands have been successfully reclaimed by a mixture of Sunn-hemp and basic slag or bone.

Moreover the humus formed in the fixation of atmospheric nitrogen by a mixture of organic matter and calcium phosphates acts as a valuable buffer in maintaining soil neutrality. Since 1935 DHAR has emphasised that in the reclamation of alkali lands by gypsum or powdered sulphur, increase in the humus content or fertility does not take place but a mixture of organic matter and calcium phosphate not only neutralizes the alkali but improves the land fertility by increase of humus and nitrogenous compounds.

In this connection it is of interest to record that F. Blasco and De La Rubia (6th Soil Science Congress Paris rapport commissions I and II page 651) have observed that the humus content of two soil samples decreased from 0.31% and 0.16% to 0.1% and 0.08% respectively in 14 years. Along with this decrease of humus, the pH markedly increased and the exchangeable calcium appreciably decreased.

#### PERMANENT RECLAMATION OF ALKALI LAND BY A MIXTURE OF PHOSPHATES AND DILUTE MOLASSES

For over 20 years, Dhar and coworkers reported that either molasses alone or a mixture of molasses and pressmud, half and half, can be readily utilized for fixing atmospheric nitrogen and reclaiming alkali soils. At present, a good deal of Indian molasses is sold to other countries and a portion is utilized in the manufacture of power alcohol. Consequently, concentrated molasses containing 50 to 60% carbohydrates is not available for manuring fields or reclaiming alkali soils. Recently, we have used dilute molasses in the form of spent wash either alone or dilute molasses mixed with phosphate in successfully reclaiming alkali soils of pH 10. The molasses used in the following experiments was dilute and contained 73% water, 6.8% carbon and 0.1% nitrogen in the liquid condition. When the specimen was oven-dried, the carbon content was raised to 25.1% and nitrogen to 0.36%. The following results were obtained in laboratory experiments :—

200 gms. soil + 9.2 gms. Spent Wash.

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available $P_2O_5$ %	Efficiency in mgm.	pH
0	1.233	0.050	...	3.572	0.030	...	10.00
90	0.858	0.053	30.4	4.402	0.041	7.5	9.70
180	0.715	0.054	42.0	5.241	0.043	8.0	9.35
270	0.593	0.054	51.9	5.712	0.045	...	9.05
360	0.496	0.054	60.0	5.986	0.046	...	8.70

200 gms. soil + 20.6 gms. Spent Wash

Period of exposure in days.	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available $P_2O_5$ %	Efficiency mgm.	pH
0	2.468	0.066	...	3.572	0.029	...	10.00
90	1.729	0.065	29.1	4.502	0.045	...	9.60
180	1.484	0.065	39.1	5.204	0.047	...	9.20
270	1.233	0.064	50.0	5.812	0.048	...	8.8
360	1.036	0.064	58.0	6.232	0.049	...	8.5

200 gms soil + 9.2 gms. Spent Wash + 0.5% North-African Rock Phosphate A

0	1.233	0.050	...	3.572	0.070	...	10.00
90	0.806	0.055	34.6	5.804	0.088	11.7	9.40
180	0.657	0.059	46.7	7.054	0.108	15.6	8.80
270	0.545	0.062	55.8	7.915	0.115	17.4	8.20
360	0.447	0.062	63.7	8.324	0.121	...	7.60

200 gms. soil + 20.6 gms. Spent Wash + 0.5% North-African Rock Phosphate A

0	2.468	0.066	...	3.572	0.066	...	10.00
90	1.610	0.068	34.8	5.824	0.095	2.4	9.40
180	1.356	0.069	45.6	7.095	0.114	2.7	8.76
270	1.117	0.068	50.5	7.954	0.121	...	8.14
360	0.914	0.063	63.0	8.402	0.127	...	7.50

200 gms. soil + 9.2 gms. Spent Wash + 1.0% North-African Rock Phosphate A.

0	1.233	0.050	...	3.572	0.105	...	10.00
90	0.806	0.056	34.6	5.824	0.125	14.0	9.40
180	0.614	0.061	50.0	7.098	0.134	17.7	8.75
270	0.535	0.063	55.8	7.922	0.142	18.6	8.20
360	0.438	0.063	64.5	8.415	0.148	...	7.56

200 gms. soil + 20.6 gms. Spent Wash + 1.0% North-African Rock Phosphate A

0	2.468	0.066	...	3.572	0.100	...	10.00
90	1.585	0.068	35.7	5.915	0.125	2.3	9.40
180	1.336	0.069	45.8	7.120	0.137	2.7	8.65
270	1.100	0.069	55.4	7.964	0.148	...	8.10
360	0.874	0.068	64.9	8.514	0.156	...	7.50

200 gms. soil + 9.2 gms. Spent Wash + 0.5% Trichinopoly Rock Phosphate

0	1.233	0.050	...	3.572	0.043	...	10.00
90	0.824	0.054	33.8	5.725	0.075	9.8	9.60
180	0.664	0.058	46.1	0.985	0.083	14.1	8.80
270	0.560	0.060	54.6	7.512	0.091	15.0	8.30
360	0.485	0.060	60.7	7.922	0.096	...	7.80

200 gms. soil + 20.6 gms. Spent Wash + 0.5% Trichinopoly Rock Phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available $P_2O_5$ %	Efficiency in mgm.	pH
0	2.468	0.066	...	3.572	0.041	...	10.00
90	1.646	0.067	33.3	5.775	0.082	1.2	9.50
180	1.384	0.068	43.9	7.095	0.092	1.9	8.80
270	1.137	0.068	53.9	7.945	0.100	...	8.30
360	0.900	0.068	63.5	8.394	0.108	...	7.70

200 gms. soil + 9.2 gms. Spent Wash + 1.0% Trichinopoly Rock Phosphate

0	1.233	0.050	...	3.572	0.053	...	10.00
90	0.814	0.055	33.9	5.754	0.088	12.0	9.55
180	0.655	0.060	46.8	6.985	0.096	17.3	8.80
270	0.551	0.062	55.3	7.542	0.103	17.6	8.25
360	0.453	0.063	63.2	8.015	0.110	17.0	7.75

200 gms. soil + 20.6 gms. Spent Wash + 1.0% Trichinopoly Rock Phosphate

0	2.468	0.066	...	3.572	0.051	...	10.00
90	1.632	0.068	34.3	5.775	0.088	2.4	9.50
180	1.372	0.069	44.5	7.126	0.099	2.8	8.80
270	1.125	0.069	54.5	7.954	0.108	...	8.20
360	0.898	0.068	63.6	8.401	0.115	...	7.73

200 gms. soil + 9.2 gms. Spent Wash + 0.5% Tata Basic Slag

0	1.232	0.050	...	3.572	0.056	...	10.00
90	0.794	0.054	35.6	5.454	0.066	9.1	9.70
180	0.644	0.056	47.8	6.715	0.075	10.2	9.30
270	0.524	0.057	57.5	7.413	0.082	9.9	8.85
360	0.435	0.057	64.7	7.812	0.090	...	8.40

200 gms. soil + 20.6 gms. Spent Wash + 0.5% Tata Basic Slag

0	2.468	0.066	...	3.572	0.053	...	10.00
90	1.586	0.067	35.7	5.542	0.074	1.1	9.60
180	1.332	0.067	46.0	6.932	0.084	...	9.16
270	1.087	0.066	56.4	7.743	0.092	...	8.65
360	0.915	0.066	62.9	8.195	0.100	...	8.20

200 gms. soil + 9.2 gms. Spent Wash + 1.0% Tata Basic Slag

0	1.233	0.050	...	3.572	0.077	...	10.00
90	0.781	0.055	36.6	5.542	0.087	11.6	9.60
180	0.632	0.057	48.7	6.765	0.109	11.6	9.10
270	0.513	0.058	58.4	7.743	0.118	11.1	8.60
360	0.438	0.058	64.5	8.215	0.126	...	8.20

200 gms. soil + 20.6 gms. Spent Wash + 1.0% Tata Basic Slag

0	2.468	0.066	...	3.572	0.073	...	10.00
90	1.586	0.068	35.7	5.742	0.105	2.3	9.60
180	1.320	0.068	46.5	6.948	0.117	...	9.05
270	1.077	0.067	56.4	7.943	0.128	...	8.50
360	0.905	0.067	63.3	8.495	0.135	...	8.00

200 gms. soil+9.2 gms. Spent Wash+0.5% Kulti Basic Slag

Period of exposure in days.	Total carbon %	Total nitrogen %	Ex-Ca in m.e. %	Efficiency in mgm.	pH
0	1.233	0.050	3.572	...	10.00
90	0.794	0.053	5.553	7.0	9.70
180	0.632	0.056	6.765	10.0	9.32
270	0.521	0.056	7.512	...	8.85
360	0.422	0.056	7.915	...	8.40

200 gms. soil+20.6 gm. Spent Wash+0.5% Kulti Basic Slag

0	2.468	0.066	3.572	...	10.00
90	1.606	0.067	5.643	1.1	9.65
180	1.295	0.067	7.035	...	9.16
270	1.062	0.065	7.784	...	8.65
360	0.889	0.065	8.234	...	8.25

200 gms. soil+9.2 gms. Spent Wash+1.0% Kulti Basic Slag

0	1.233	0.050	3.572	...	10.00
90	0.769	0.054	5.553	9.0	9.65
180	0.621	0.057	6.765	11.4	9.16
270	0.508	0.057	7.642	...	8.65
360	0.397	0.057	8.132	...	8.25

200 gms. soil+20.6 gms. Spent Wash+1.0% Kulti Basic Slag

0	2.468	0.066	3.572	...	10.00
90	1.581	0.068	5.742	2.3	9.60
180	1.259	0.067	7.035	...	9.10
270	1.037	0.067	7.785	...	8.83
360	0.865	0.067	8.335	...	8.15

The foregoing results clearly show that in this process, the exchangeable calcium and available phosphate markedly increase with the lapse of time, chiefly due to the formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and in small amounts  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ . The pH falls off markedly and tends to be that of normal soil. Moreover the humus and the nitrogen status appreciably increase, thus increasing the fertility of the land.

During the last 25 years, all over India bad alkali lands have been reclaimed and brought under cultivation by molasses or a mixture of molasses and press mud. Molasses mixed with different phosphate rocks or bones on basic slag has been found to be highly effective in alkali soil reclamation.



# INDUSTRIALLY BACKWARD COUNTRIES NEGLECT PHOSPHATE FERTILISATION

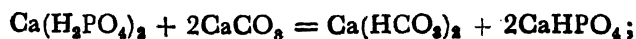
It has been emphasised in the publications from this Laboratory that for permanent agriculture it is profitable to increase the phosphate status of land under cultivation, because, phosphates help markedly in the fixation of atmospheric nitrogen by the oxidation of plant residues and other organic substances present in the soil. Moreover phosphates maintain soil neutrality. In the following table the ratios of N/P consumed in various countries of the world have been tabulated. The results show that the economically backward countries do not pay attention to the enrichment of land with phosphate fertilizers, but, for producing more cereals, nitrogen manuring is carried on. This practice does not improve land fertility at all. On the other hand, many economically advanced countries utilize more phosphatic fertilizers than nitrogenous ones.

		$\frac{N}{P_2O_5}$			
Germany	... $\frac{571384}{564117}$	1.01	: 1	Peru	... $\frac{19392}{16408}$ 1.2 : 1
U. S. A.	... $\frac{334603}{675223}$	1	: 2.01	Eire	... $\frac{6765}{26717}$ 1 : 3.9
France	... $\frac{154770}{353274}$	1	: 2.2	Switzerland	... $\frac{3911}{24219}$ 1 : 6.2
U. S. S. R.	... $\frac{139892}{386731}$	1	: 2.7	Norway	... $\frac{7191}{14369}$ 1 : 1.99
Japan	... $\frac{252824}{232909}$	1.07	: 1	Latvia	... $\frac{3767}{22923}$ 1 : 6.08
Italy	... $\frac{116229}{219486}$	1	: 1.9	Dutch East Indies	... $\frac{18864}{11413}$ 1.6 : 1
Netherlands	... $\frac{62081}{100858}$	1	: 1.6	Puerto Rico	... $\frac{14446}{4626}$ 3.1 : 1
U. K.	... $\frac{50790}{180472}$	1	: 3.5	China	... $\frac{27035}{480}$ 55.4 : 1
Spain	... $\frac{103727}{165565}$	1	: 1.6	Hawaii	... $\frac{13612}{32}$ 425 : 1
Australia	... $\frac{12550}{249595}$	1	: 19.8	Austria	... $\frac{5184}{12832}$ 1 : 2.4
Belgium	... $\frac{52181}{81087}$	1	: 1.5	Lithuania	... $\frac{1319}{18085}$ 1 : 13.7
Poland	... $\frac{26109}{32872}$	1	: 1.2	Ceylon	... $\frac{8468}{9119}$ 1 : 1.07
Denmark	... $\frac{40542}{67163}$	1	: 1.6	India	... $\frac{16288}{1612}$ 10.1 : 1

Sweden	...	$\frac{27690}{50917}$	1 : 1.8	Algeria	...	$\frac{3145}{12134}$	1 : 3.8
Korea	...	$\frac{93690}{21017}$	10.4 : 1	Greece	...	$\frac{5211}{7376}$	1 : 1.4
New Zealand	...	$\frac{4276}{101903}$	1 : 2.3	Estonia	...	$\frac{911}{10396}$	1 : 11.4
Czechoslovakia	...	$\frac{24852}{48646}$	1 : 1.9	Hungary	...	$\frac{2333}{10371}$	1 : 4.4
Egypt	...	$\frac{73733}{8955}$	8.2 : 1	Canary Islands	...	$\frac{4521}{2653}$	1.7 : 1
Canada	...	$\frac{14738}{33953}$	1 : 2.3	Philippines	...	$\frac{6649}{108}$	61.5 : 1
South Africa	...	$\frac{9112}{41383}$	1 : 4.5	Yugoslavia	...	$\frac{1668}{4397}$	1 : 2.6
Finland	...	$\frac{7866}{28741}$	1 : 2.6	Mexico	...	$\frac{2802}{0}$	...
Formosa	...	$\frac{34180}{13970}$	2.4 : 1	Brazil	...	$\frac{1938}{0}$	...
Portugal	...	$\frac{15928}{32865}$	1 : 2.06	All others	...	$\frac{30947}{25764}$	1 : 0.8

#### REACTION OF SUPERPHOSPHATES ON SOILS

The superphosphate industry depends on the action of sulphuric acid on apatites forming a mixture of the sparingly soluble calcium sulphate and the readily soluble monocalcium phosphate almost half in weight of the calcium sulphate, with liberation of hydrofluoric acid which reacts with silica and forms  $\text{H}_2\text{SiF}_6$  gas. When superphosphate is added to a neutral soil containing calcium carbonate, there is formation of a mixture of sparingly soluble tri- and di-calcium phosphates according to the following equations:—



Hence in these processes small amounts of calcium, i.e. equivalent to the calcium introduced in superphosphate as calcium monophosphate may be washed away when rain falls. Consequently, under certain conditions, the lime requirement of such a soil may slightly increase temporarily. On the other hand, when superphosphate is added to acidic soils containing ferric and aluminium or titanium ions, there is the formation of very sparingly soluble phosphates of iron, aluminium and titanium and liberation of mineral acids in the soil causing a marked increase in the soil acidity and lime requirement. This explains the results obtained by Skinner and Beattie working at the Arlington, Virginia, farm of the U. S. Department of Agriculture, who reported that the lime requirement of the surface

6 inches of the soil was increased following five annual applications of superphosphate at the rate of 200 lbs. per acre.

The newly or freshly formed tri- and di-calcium phosphate is much more soluble in water or carbonic acid or nitric acid obtained in the nitrification of proteins and other nitrogenous compounds present in the soil. Consequently the superphosphate-treated soil can more readily yield available phosphate to plants than the apatite or the sedimentary phosphate rock containing aged and inactive calcium phosphate. This is an important point in favour of the use of superphosphate or other soluble phosphatic fertilizers in preference to finely-divided phosphate rocks.

The solubility of phosphorus in the soil is determined by the type of phosphate added but is low in all soils. The favourable conditions for solubility are (a) a large amount of organic matter undergoing oxidation (b) slightly acidic pH level, (c) a high phosphate content of the soil, (d) adequate moisture status and (e) a high  $\frac{\text{silica}}{\text{sesquioxide}}$  ratio.

Most cultivated lands of temperate countries contain an average of 10 lbs. available  $P_2O_5$  per acre with a variation of 5 to 20 lbs.

### SOILS POOR IN LIME CAN BECOME ACIDIC BY SUPERPHOSPHATES

There has been considerable controversy regarding the power of superphosphate in increasing the acidity of soils. This is clear from the following lines :—

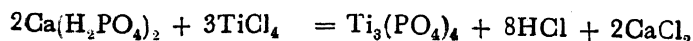
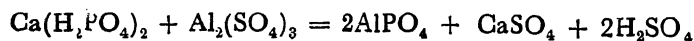
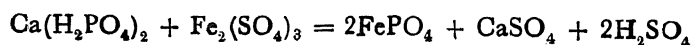
Skinner and Beattie in 1917, working at the Arlington, Virginia, farm of the United States Department of Agriculture, reported that the lime requirement of the surface 6 inches of the soil was increased following 5 annual applications of superphosphate at the rate of 200 lbs. per acre; but, Burgess (1922) of the Rhode Island Experiment Station concluded that there is no foundation for the statement that soils will become acidic following the continuous use of superphosphate. His results, which show the accumulated influence for a period of 27 years, are recorded below :—

#### *Relative Influence of the continued use of various Phosphates on the Lime requirement of soil.*

	Total crop grown last 5 years. (tons)	Lime requirement ( Jones Method) Lbs. CaO per acre
Check .....	17.6	2700
Floats.....	29.4	2520
Superphosphate .....	31.5	2346
Extra superphosphate.....	42.2	2250
Ground bone.....	33.4	2160
Thomas slag.....	32.7	2070

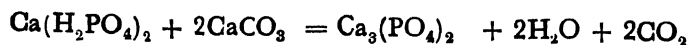
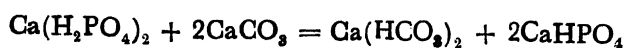
The discrepancy between the results of Skinner and Beattie and Burgess is explained in the following manner : When superphosphate is added to an acid

soil very poor in calcium carbonate, the superphosphate is likely to react on the soluble salts of Fe, Al and Ti according to the following equations :—



It is clear, therefore, that in such acid soils the liberation of sulphuric or other mineral acids makes the soil more acidic and their lime requirement markedly increases. This may explain the observations of Skinner and Beattie who reported an increase of soil acidity by fertilizing with superphosphate.

On the other hand, with soils rich in calcium carbonate, superphosphate causes the following reactions to take place :—



In certain cases, small amounts of calcium, that is equivalent to the calcium introduced in the superphosphate existing as calcium monophosphate, may be washed away from the soil as  $\text{Ca}(\text{HCO}_3)_2$ . But, because,  $\text{CaHPO}_4$  is sparingly soluble and is not as readily converted into soluble calcium monophosphate by the action of carbonic acid as the ready conversion of calcium carbonate to the soluble bicarbonate by the action of carbonic acid in soil, the acidity and the lime requirement of a soil may decrease. This viewpoint has been recently emphasised in our previous publications and it has been clearly established that addition of soluble and insoluble phosphates decreases the leaching of lime and hence the lime requirement of such a soil decreases.

The possibility of the formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in the soil from tricalcium phosphate and hydrogen ions is greater than the generation of  $\text{Ca}(\text{HCO}_3)_2$  from calcium carbonate and hydrogen ions. The fact that  $\text{Ca}(\text{HCO}_3)_2$  is much more soluble than  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is of very great importance in saving lime in soils when phosphates are added and maintaining soil neutrality.

## VALUE OF SOFT PHOSPHATE ROCKS IN CROP PRODUCTION

In recent years a large amount of investigation and field trials are going on all over the world for utilising finely-divided phosphate rocks by direct addition without conversion to superphosphate for crop production, but, erratic results have been reported. There is no doubt that for acid soils good results have been obtained all over the world with finely divided phosphate rocks. Russell has reported an increased yield of 26% with the North-African (Gafsa) phosphate whilst superphosphate showed an increased yield of 29.6% whilst in other experiments the same rock phosphate caused an increased yield of about 45% and superphosphate

47%. The North-African Company of Hyperphosphate (Reno) deal with Gafsa phosphate having the following composition :—

Water combined with organic matter	...	3.49
H <sub>2</sub> SO <sub>4</sub>	... ..	2.79
Phosphoric acid	... ..	30.50
Carbonic acid	... ..	5.41
Silicic matter	... ..	3.34
Iron oxide	... ..	0.72
Aluminium	... ..	0.52
Chalk	... ..	46.76
Magnesium	... ..	0.83
Potassium	... ..	0.11
Sodium	... ..	0.92
Fluorine	... ..	2.35
Chlorine	... ..	0.06
Total	...	100.89
Subtract oxygen corresponding to fluorine and chlorine	...	0.98
		99.91

Favourable results by direct addition of this phosphate rock have been reported from different parts of the world.

It is well known that a very large number of experiments have been carried on by the Illinois University and other workers in U. S. A., U. S. S. R., Finland, Poland, Ireland and other countries, and, they recommend the use of finely-divided phosphate rocks in permanent agriculture. In this connection, the following lines by Waggaman are of interest: "In order to maintain the fertility of soils indefinitely with respect to phosphoric acid, a number of agronomists and agricultural chemists recommend the application of finely ground unacidulated raw rock phosphate directly on the field. The mineral phosphates of the soil, which normally support plant life, probably have no greater solubility than phosphate rock. In fact, iron and aluminium phosphates, often the chief compounds of phosphoric acid in soils, are no more soluble than phosphate rock which is known to be appreciably dissolved by carbonated waters and, therefore, should enter the soil solution which is nearly always rich in CO<sub>2</sub>.

The agricultural value of finely-ground unacidulated mineral phosphates does not lack practical supporting evidence. Many experiments conducted in the laboratory, green house and field, point strongly to the merit of this material and a compilation and classification of many long time experiments conducted with raw rock phosphates (W. H. Waggaman & C. R. Wagner, U. S. Dept. of Agr. Bull. No. 699, 1948) led to the conclusion that this material usually

increased crop yields. From a financial standpoint, the results obtained often compared favourably with those from other types of phosphatic fertilizers. Very fine grinding, liberal application and the presence of the substantial amounts of organic matter in the soil are important factors in determining the effectiveness of raw ground phosphate rock as a fertilizer. R. P. Bartholomew (J. Amer. Soc. Argon. 29, 293, 1937), in studying the effect of ground phosphate rock on soils of varying acidity, concluded that the availability of  $P_2O_5$  decreased as the fluorine content increased. However, even when all conditions are favourable for its utilization, this product should not be expected to give as quick returns as the more soluble phosphatic fertilizers".

In previous publications it has been emphasised that all sparingly soluble phosphates undergo copious hydrolysis. Tricalcium phosphate is hydrolysed in the following way:  $4Ca_3(PO_4)_2 + 6H_2O = 3Ca_3(PO_4)_2 + Ca(OH)_2 + 2H_3PO_4$ . Consequently, a fair amount of phosphoric acid is available in water treated with calcium phosphate.

Ordinarily dicalcium phosphate exists in the anhydrous state as  $CaHPO_4$  and in another form as  $CaHPO_4 \cdot 2H_2O$ . The anhydrous salt is less soluble than the tricalcium phosphate whilst the hydrated dicalcium phosphate is more soluble than the tricalcium phosphate. This is shown in Rindell's data in which  $CaHPO_4 \cdot 2H_2O$  liberates 1.44 milli-mole  $CaO$  and 1.19 milli-mole  $P_2O_5$  at  $20^\circ$  per litre whilst 0.7 milli-mole  $CaO$  and 0.61 milli-mole  $P_2O_5$  per litre are liberated from  $CaHPO_4$ . It seems therefore, that in soils dicalcium phosphate ( $CaHPO_4 \cdot 2H_2O$ ) is likely to be present in larger amounts than tricalcium phosphate when soils are phosphated either by superphosphate or finely-divided phosphate rocks. But, in course of time, due to the presence of fluorine in all soils, the calcium phosphates have a tendency to pass into the very sparingly soluble fluor-apatites.

In the following table the fluorine contents and the percentage solubility of  $P_2O_5$  in citric acid of some naturally occurring phosphate rocks have been recorded :—

Source	Total $P_2O_5$ %	Percent solubility $P_2O_5$ in citric acid	Fluorine %
Cheriton Java.	29.7	43	0.2
Christmas Island.	38.3	40	1.1
Curacao.	34.0	24	0.4
England (Taplow phosphate chalk).	13.9	2	1.2
Egypt Safaga.	28.7	39	4.0
Safi.	30.8	35	3.5
Nauru Island.	35.6	26	2.5
Nigeria.	23.6	3	0.9
North Africa.			
Algeria (Constantine).	24.8	—	—
Morocco.	32.5	34	3.3
Tunis (Gafsa).	27.8	40	3.4
Rhodesia.	31.3	—	—
Uganda (Tororo).	25.6	16	2.0
U. S. A. (Florida pebble phosphate).	33.5	18	3.7
U. S. S. R. (Kola Concentrate).	40.3	9	3.0
Steamed bone meal.	34.2	78	—

The foregoing data show that there is no relationship between the fluorine content and the percentage solubility of  $P_2O_5$  in citric acid.

Further research is necessary to determine quantitatively the factors which control the solubility and availability of the various rock phosphates, basic slags and other sources of phosphates.

G. W. Cooke (Empire Journal of Experimental Agriculture Vol. XXIV (1956), 295) has reported the following values of recovery of phosphates :—

Percentage of added phosphates recovered.

From	Crop 1	Crop 2	Crop 1+2
Superphosphate	52	6	58
Gafsa	19	27	46
Morocco	14	20	34
Safi (coarse)	12	13	25
„ (normal)	9	15	24

Comparisons of Basic slag, Morocco phosphate and monocalcium phosphate for several crops.

Crop		Bessemer Slag	Morocco rock phosphate % monocalcium phosphate equivalent
Swedes	...	80	50
Rape	...	70	65
Mustard	...	105	15
Radish	...	125	120
Clover	...	90	20
Rye grass	...	55	20
Timothy	...	75	0
Wheat	...	100	10
Barley	...	100	15
Rye	...	85	5
Buck Wheat	...	85	45
Lettuce	...	70	0

Percentage recovery of added phosphates by turnips in pots.

	Acid Soil pH 5.7	Alkaline Soil pH 7.8
Superphosphate	22	13
Basic slag	19	9
Gafsa	16	2
Curacao	9	4
Taplow	2	1

The foregoing results show that like basic slag, which has been found to be a valuable source of phosphate all over the world, direct addition of the North African phosphate rocks is profitable in several crop production.

Moreover Cooke has reported that the following amounts of rock phosphates became soluble when wheat straw was incubated at 30° for 1 month with and without rock phosphates and the pH of the mixture was 4.6 :—

From	% of added phosphorus rendered water soluble
Gafsa	7
Curacao	8
Florida	3

Similar results have been obtained by us in our experiments by mixing different organic substances with soil and phosphates as reported in the foregoing pages.

**CaHPO<sub>4</sub>·2H<sub>2</sub>O MORE SOLUBLE THAN Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> WHICH PRODUCES MORE PHOSPHORIC ACID IN WATER THAN CaHPO<sub>4</sub>**

On page 59 of Rindells Book (Untersuch, Loslichkeit Kalk phosphate, Helsingfors 1899) the solubility of CaHPO<sub>4</sub>·2H<sub>2</sub>O is recorded at different temperatures and the values are as follows :—

Temperature	CaO (millimole)	H <sub>3</sub> PO <sub>4</sub> (millimole)	H <sub>3</sub> PO <sub>4</sub> /CaO
24.5°	...	1.44	2.36
30°	...	1.70	2.91
40°	...	2.78	4.48
50°	...	4.67	8.70
60°	...	7.76	14.83
68°	...	6.09	11.61
72.9°	...	5.63	10.73
100.1°	...	5.55	10.69
			1.64
			1.71
			1.74
			1.86
			1.91
			1.91
			1.91
			1.93

On the other hand, the solubility of CaHPO<sub>4</sub> at different temperatures has been found by Rindell to be as follows :—

CaHPO <sub>4</sub>			
Temperature	CaO (millimole)	H <sub>3</sub> PO <sub>4</sub> (millimole)	H <sub>3</sub> PO <sub>4</sub> /CaO
30°C	...	0.74	1.22
40°	...	1.05	1.92
50°	...	1.19	2.30
60°	...	1.29	2.46
68°	...	1.76	3.15
72.9°	...	1.84	3.49
100.1°	...	1.87	3.47
			1.65
			1.83
			1.94
			1.91
			1.71
			1.89
			1.86



The foregoing results of Rindell clearly show that the anhydrous  $\text{CaHPO}_4$  is much less soluble than  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . But one thing is very clear that the ratio of  $\text{H}_3\text{PO}_4/\text{CaO}$  in both the salts changes practically in the same way with increasing temperature. The ratio changes from 1.64 to 1.93 in the case of  $\text{CaHPO}_3 \cdot 2\text{H}_2\text{O}$  whilst with the anhydrous salt the ratio varies from 1.65 to 1.86 showing that increase in hydrolysis is not very pronounced.

On the other hand, Rindell, on page 68, has recorded the following solubility of  $\text{Ca}_3(\text{PO}_4)_2$  with the formula  $2.90_2\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 4.87\text{H}_2\text{O}$ .

Temperature	CaO (millimole)	$\text{H}_3\text{PO}_4$ (millimole)
30° C	0.07	1.85
50°	0.07	2.72
60°	0.07	2.60
68°	0.04	5.13
72.9°	0.13	3.27
99.7°	...	2.59

The foregoing results with tricalcium phosphate very clearly show that the trisalt is much less soluble than the di-salt containing  $2\text{H}_2\text{O}$ . The amount of  $\text{P}_2\text{O}_5$  existing in the state of solution from the triphosphate at 30° and higher temperatures is appreciably higher than the  $\text{P}_2\text{O}_5$  present in a saturated solution of  $\text{CaHPO}_4$ , but, the amount of  $\text{P}_2\text{O}_5$  available from  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  at all temperatures is much greater than with the triphosphate. The availability of the triphosphate in presence of carbonic acid is appreciably increased due to the formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in the soil by the action of  $\text{H}_2\text{CO}_3$  on  $\text{Ca}_3(\text{PO}_4)_2$ . The data of Rindell given on page 68 regarding the amount of CaO present in the state of solution show that this is 1/10th. of that present in the solution of  $\text{CaHPO}_4$  and 1/20th. of that from  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . It is clear, therefore, that if the solubility of tricalcium phosphate in water is estimated by the analysis of the amounts of lime present the solubility of tricalcium phosphate appears to be 1/20th. of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . Actually old investigators must have done the same thing and that is why the solubility of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  has been found to be 20 times that of  $\text{Ca}_3(\text{PO}_4)_2$ . On the other hand, from the phosphate point of view at 30° the amounts of  $\text{P}_2\text{O}_5$  are as follows :—

$\text{Ca}_3(\text{PO}_4)_2$	1.85	millimoles	$\text{H}_3\text{PO}_4$
$\text{CaHPO}_4$	1.22	"	"
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	2.91	"	"

With increasing temperature the amounts of  $\text{P}_2\text{O}_5$  increase much less with both  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaHPO}_4$  than with  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . It is interesting to note that Rindell has shown that the triphosphate has more or less the same solubility regarding lime at temperatures varying from 30° to 60°. The solubility of  $\text{H}_3\text{PO}_4$  is changed to a greater extent than that of lime with increase of temperature, but, the changes are haphazard. Moreover, the foregoing results clearly show that when tricalcium phosphate is shaken with water, it is highly hydrolysed forming monocalcium phosphate and phosphoric acid in solution. Dicalcium phosphate on hydrolysis produces monocalcium phosphate in solution but the hydrolysis is less developed than with tricalcium phosphate.

It has been reported that the solubility of tricalcium phosphate increases considerably when increasing amounts of the solid are shaken with same amount of water. Moreover, in presence of small amounts of phosphoric acid its solubility is greatly increased. There is no doubt that this behaviour is chiefly due to the marked hydrolysis of tricalcium phosphate in presence of water, and, there is appreciable amount of monocalcium phosphate and perhaps free phosphoric acid in an aqueous solution of tricalcium phosphate and that is why the aqueous solution obtained by treating distilled water is feebly acidic. When calcium carbonate is

added to tricalcium phosphate the hydrolysis is considerably checked and the amount of phosphate passing into solution is much less. This is evident from the following results obtained by us at 25°

	gms. $P_2O_5$ in the extract after shaking for 2 hours & filtering after 24 hours.
1 gm. $P_2O_5$ of $Ca_3(PO_4)_2$ + 100 c.c. water	0.0204
1 gm. $P_2O_5$ of $Ca_3(PO_4)_2$ + 0.2 gm. $GaCO_3$ + 100 c.c. water	0.00139

Similarly, the hydrolysis of ferric phosphate is appreciably checked by adding  $CaCO_3$  as is evident from the following observations :—

	gms. $P_2O_5$ in the extract after shaking for 2 hours and filtering after 24 hours.
1 gm. $P_2O_5$ of $FePO_4$ + 100 c.c. water	0.0041
1 gm. $P_2O_5$ of $FePO_4$ + 0.02 gm. $CaCO_3$ + 100 c.c. water	0.00093

We have observed that precipitated calcium carbonate slowly reacts with ferric phosphate forming brown ferric hydroxide and calcium phosphate which is much more soluble than ferric phosphate.

#### CARBONIC ACID HELPS PHOSPHATE LIBERATION FROM CALCIUM PHOSPHATES BUT NOT FROM FERRIC PHOSPHATE

When carbonic acid is passed through suspensions of basic slag, rock phosphate,  $Ca_3(PO_4)_2$  and  $CaHPO_4$ , the amount of  $P_2O_5$  passing into solution increases. This is evident from the following results :—

	$P_2O_5$ in millimoles per litre after 7 days.	
(a) { 0.5 gm. $P_2O_5$ of basic slag + 100 c.c. water ... 0.007		
{ 0.5 gm. $P_2O_5$ of basic slag + 100 c.c. water and $CO_2$		
passed for 7 days ... 0.017		
(b) { 0.5 gm. $P_2O_5$ of rock phosphate + 100 c.c. water ... 0.005		
{ 0.5 gm. $P_2O_5$ of " " + 100 c.c. water and		
$CO_2$ passed for 7 days ... 0.017		
		CaO
(c) { 1 gm. $P_2O_5$ of $Ca_3(PO_4)_2$ + 100 c.c. water ... 1.40		2.0
{ 1 gm. $P_2O_5$ of $Ca_3(PO_4)_2$ + 100 c.c. water and $CO_2$		
passed for 7 days ... 1.64		2.31
(d) { 1 gm. $P_2O_5$ of $CaHPO_4$ + 100 c.c. water ... 0.40		0.75
{ 1 gm. $P_2O_5$ of $CaHPO_4$ + 100 c.c. water and $CO_2$		
passed for 7 days ... 0.50		1.0

It appears that as 3 to 5% lime is present in basic slag, a part of the carbonic acid introduced into the system is utilized in forming  $CaCO_3$  whilst another part reacts with  $Ca_3(PO_4)_2$  present in basic slag forming  $CaHPO_4 \cdot 2H_2O$ . On the other hand, with rock phosphate the amount of free phosphoric acid in aqueous solution is smaller than in basic slag, but, on passing  $CO_2$  the whole of the carbonic acid reacts with the tricalcium phosphate and forms dicalcium phosphate.

When carbonic acid is passed in water containing a suspension of basic slag for a long time, it passes into solution and in the following table the results obtained by Reis and Arens show the relative solubility of several slags and various other phosphate-bearing materials in water saturated with  $CO_2$ . It will be noted that in most instances the  $P_2O_5$  in the slags has a much higher solubility than that in bone, phosphorite or even dicalcium phosphate.

*Solubility of Basic Slag in water saturated with Carbonic Acid.*

Content of	Quantities dissolved by 10 Litres of water saturated by CO <sub>2</sub>					Comparative solubility			Molar ratio of CaO & P <sub>2</sub> O <sub>5</sub> in the dis- solved state
	SiO <sub>2</sub> %	P <sub>2</sub> O <sub>5</sub> %	CaO %	SiO <sub>2</sub> %	P <sub>2</sub> O <sub>5</sub> %	CaO %	SiO <sub>2</sub> %	P <sub>2</sub> O <sub>5</sub> %	
Basic slag I	2.57	18.30	48.68	1.51	4.19	19.37	58.8	22.9	39.8
Basic slag II	5.20	15.07	48.82	3.15	5.66	24.84	50.9	37.4	51.0
Basic slag III	2.85	21.30	48.36	2.11	7.55	27.85	74.0	35.5	57.5
Basic slag IV	4.05	18.33	50.35	2.27	6.81	24.19	56.0	37.5	48.0
Basic slag V	7.67	16.32	47.98	4.22	7.89	24.54	56.3	48.1	51.1
Basic slag VI	6.93	15.74	48.15	3.55	4.50	25.08	51.2	28.7	52.0
Basic slag VII	5.54	24.00	46.35	3.05	7.59	19.36	86.1	31.6	41.7
Shell slag	18.15	13.47	44.10	4.99	3.45	15.17	27.4	25.5	34.4
Prepared slag	6.58	24.95	51.25	4.07	7.79	21.00	61.8	31.2	40.9
Scheibler's precipitate	8.02	33.36	31.10	0.62	7.36	9.37	7.7	22.0	30.1
Heyermann's precipitate	5.70	14.93	34.05	1.29	4.96	19.96	22.7	33.0	58.5
Dicalcic phosphate of lime	...	51.09	41.03	...	8.57	6.95	...	16.8	16.8
Tricalcic phosphate of lime	...	43.26	51.45	...	5.41	7.04	...	12.5	13.6
Tetracalcic phosphate of lime	...	36.85	62.70	...	15.52	33.27	...	42.1	53.0
Degreased cattle bones	...	25.23	32.75	...	7.19	9.65	...	28.5	28.9
Bone ash made from above bones	...	41.71	55.75	...	2.29	3.29	...	5.5	5.9
Phosphorite	1.77	32.00	45.36	0.10	1.00	1.67	5.7	3.1	3.8

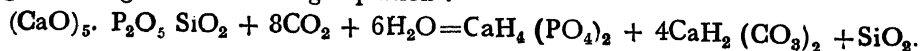
The foregoing results show that in the dissolved condition by introducing  $\text{CO}_2$  more lime than phosphoric acid exists in the system.

On the other hand, Rindell has recorded the following values on the action of carbonic acid on tricalcium and dicalcium phosphates :—

		$\text{Ca}_3(\text{PO}_4)_2$							
	$\text{CO}_2$	...	1.95	3.91	7.81	15.63	millimole/litre		
	$\text{CaO}$	...	2.7	52.5	4.2	11.0	do. do.		
	$\text{P}_2\text{O}_5$	...	0.11	0.10	0.17	0.44	gm/litre		
	$\text{P}_2\text{O}_5$	...	3.32	2.90	1.77	3.30	gm/litre		
	$\text{P}_2\text{O}_5$	...	23.7	20.4	12.5	23.5	millimole/litre		
		$\text{CaHPO}_4$					$\text{CaHPO}_4 : 2\text{H}_2\text{O}$		
millimole	$\text{CO}_2$	...	1.95	3.91	7.81	15.63	1.95	3.91	7.81
per litre.	$\text{CaO}$	...	0.93	1.04	1.54	2.32	1.67	1.71	1.92
	$\text{P}_2\text{O}_5$	...	1.24	1.31	1.85	2.40	2.65	2.50	2.20
							2.20	2.98	

In these results much more phosphoric acid than lime has been found in the dissolved condition by passing carbonic acid. Further work is needed to clear up the situation.

Moreover, Lyon & Buckman have reported that carbonic acid reacts on basic slag according to the following equation :—



#### DIFFERENT TYPES OF BASIC SLAGS SUITABLE FOR CROP PRODUCTION

It is well known that basic slag which is a bye-product of the expanding steel industry of the world ranks next to superphosphate as the world's leading phosphatic fertilizer. It is interesting that, in general, the iron ores of Europe are richer in  $\text{P}_2\text{O}_5$  than those of India or U.S.A. Hence, the amount of  $\text{P}_2\text{O}_5$  in many European basic slags vary from 17—20%  $\text{P}_2\text{O}_5$ , whilst in U. S. A. the  $\text{P}_2\text{O}_5$  content of basic slags is of the order of 8-10%. In India, the Tata Steel Works are producing one million tons of basic slag containing 8-10%  $\text{P}_2\text{O}_5$ . The analyses of Tata Slag as well as those of the rock phosphates of India are recorded below:—

<i>Chemical Analyses of Rock Phosphates and Basic Slag</i>				
Constituents	Trichinopoly Rock Phosphate Madras I %	Trichinopoly Rock Phosphate (II) %	Bihar Rock Phosphate %	Tata Basic Slag %
$\text{SiO}_2$	30.45	6.3	5.52	23.66
$\text{Fe}_2\text{O}_3$	24.31	4.2	3.92	16.75
$\text{Al}_2\text{O}_3$	12.63	26.5	23.12	
$\text{P}_2\text{O}_5$	19.86	27.5	27.9	7.59
$\text{CaO}$	11.62	20.8	11.8	34.37
$\text{MgO}$	0.60	1.75	0.30	5.29
$\text{SO}_3$	1.00	1.50	1.20	
Fluorine	0.85	0.89	0.75	
Chlorine	0.031	0.056	0.03	
$\text{K}_2\text{O}$				9.07
Available $\text{P}_2\text{O}_5$				4.46

The slag obtained from the Steel Works at Kulti near Asansol is poorer in  $P_2O_5$ , the result of the analysis being as follows:—

Slag produced per annum.....35,000 to 40,000 tons.

<i>Analysis %</i>			
$SiO_2$	...	...	15—22
$Al_2O_3$	...	..	4—7
$CaO$	...	...	43—50
$MgO$	...	...	5—7
$MnO$	...	...	4—6
$P_2O_5$	...	...	3—5
Total Fe	...	...	9—17

Germany was the greatest producer of basic slag before the World War II. Five million tons of slag were produced in this country and largely used in crop production. A typical analysis of a German slag is recorded below:—

%			
$P_2O_5$	...	...	11—23
$SiO_2$	...	...	3—13·0
$CaO$	...	...	38—59·0
$Fe_2O_3$	...	...	6—25·0
$MnO_2$	...	...	1—6·0
$Al_2O_3$	...	...	0·2—3·7
$MgO$	...	...	2·0—8·0
S.	...	...	0·2—11·4

U. S. A. consumes only 40 thousand tons of basic slag. A typical American slag has the following analysis:—

%			
$P_2O_5$	...	...	11·01
$SiO_2$	...	...	10·16
$CaO$	...	...	42·6
$MgO$	...	...	6·15
$MnO$	...	...	3·78
$Fe_3O_4$	...	...	24·0
$Al_2O_3$	...	...	0·45
$TiO_2$	...	...	0·17
$K_2O$	...	...	0·14
$Na_2O$	...	...	0·6
S	...	...	0·09

Zu, Cu, B are present in TRACES

The three principal types of slags used in modern agriculture are : Blast Furnace slag, Basic slag and the Slag obtained in the production of phosphorus in the rock phosphate reduction furnaces. Basic slag is valuable not only as an important source of phosphate but can be used in neutralising soil acidity whilst the other two slags are used chiefly for liming the land.

Blast Furnace slag is a bye-product of pig iron manufacture in which iron ore, coke or limestone or dolomite is melted at a blast furnace at 3500°F. In this process  $\text{CO}_2$  escapes and the lime or  $\text{MgO}$  and lime form silicates and the molten slag, which is light, is tapped off. This is air-cooled or quenched with water for granulation. The granular form is added directly to the soil as such whilst the water-cooled variety has to be powdered before it can be used in agriculture. The Blast Furnace slag contains very little  $\text{P}_2\text{O}_5$ , but, is a valuable liming material as its neutralising value is of the order of 75—90% of the same weight of limestone.

In actual agricultural practice, it is as good as limestone. In 1950 the production of Blast Furnace slag in U. S. A. was 35800000 tons, but, for agriculture only 83000 tons were utilized. The majority of it was utilized as rail-road ballast and manufacture of cement bricks, insulating material etc. In the following table the amounts of rare elements present in some of these slags are recorded :—

Type of slag	Pounds per ton					
	Mn	B	Zn	Cu	Co	Mo
Blast furnace	13	0.24	0.02	0.02	...	...
Domestic basic	47	0.04	0.04	0.04	0.004	0.02
Imported basic	57	0.02	0.01	0.03	0.002	0.008
Phosphorus furnace	2	0.04	0.04	0.02	...	...

An average sample of a blast furnace slag of U. S. A. possesses the following composition :—

	%	
$\text{SiO}_2$	...	33—42
$\text{CaO}$	...	36—45
$\text{MgO}$	...	3—12
$\text{Al}_2\text{O}_3$	...	10—16
$\text{FeO}$	...	0.3—2.0
$\text{MnO}$	...	0.2—1.5
S	...	1—3

Basic slag is obtained as a bye-product of the Basic Bessemer and Basic Open Hearth processes of Steel Manufacture, from pig iron produced from phosphorus-rich iron ores.

The slag contains 8—18%  $P_2O_5$ , most of which is soluble in neutral ammonium citrate or 2% citric acid solution and is highly suitable for crop production and this is largely used in Germany, France, England and other north-west European countries. When fluorspar is used as a flux in steel industry by the open hearth process, the solubility of the  $P_2O_5$  caused by the formation of a fluoroapatite becomes less and such a slag is less valuable than one free from fluorine.

As a bye-product in the manufacture of phosphorus, by melting phosphate rock with silica and coke in electric furnace, calcium silicate slags are produced. The water quenched slag is manufactured in the form of glassy, porous, brittle particles by quenching the molten material with jets of water. Various greenhouse experiments and fillers show that this material is a good source of  $P_2O_5$  and its liming value varies from 64—99% of  $CaCO_3$ . But only 185139 tons were produced by the Tennessee Valley Authority in 1953. The average composition is as follows :—

CaO 42.6—54.3%,  $SiO_2$  35.8—42.3%,  $P_2O_5$  0.93—2.30%, F 2.16—3.2%; besides varying small percentages of Al, Fe, Mg, Mn, S and other elements.

In crop production all over the world, basic slag has been found to be more efficient than rock phosphate. This is evident from the following observations :—

“Results obtained at the Kentucky Experiment Station indicate that basic slag is 85 to 100 per cent as effective as superphosphate. The relative effectiveness of different phosphates, including basic slag, as determined at the Indiana Experiment Station by Reed and Hall in 1930, and Wiancko in 1928, are given in the following table. All plots were manured and limed. Superphosphate, basic slag and steamed bonemeal were applied at the rate of 48 lbs. of phosphoric acid per acre, and phosphate rock at the rate of 192 lbs. of phosphoric acid per acre, with manure for each cover crop. The rotation consisted of corn, soybeans, wheat and clover :—

*Relative Effectiveness of Different Phosphates.*

Source of phosphorus		Cost of Fertilizer (Dollars)	Not returns per acre per rotation (Dollars)
Superphosphate	...	3.36	13.53
Steamed bonemeal	...	3.36	9.20
Basic slag	...	3.36	13.13
Phosphate rock	...	4.48	7.10
No phosphorus			

From our experimental results on the marked influence of different calcium phosphates and basic slag on the nitrogen fixation when fresh cow dung is allowed to undergo slow oxidation, we are convinced that phosphates should always be added when farm yard manure or green manure is incorporated in the soil. It is well known that on adding dung there is increase in the land fertility and in the

nitrogen status of the soil. Consequently, when a mixture of dung or farm yard manure and bone or basic slag or finely powdered phosphate rock or superphosphate is used instead of dung or farm yard manure alone as has been done in the classical Rothamsted experiments where the nitrogen status of the land was raised from 0.122% to 0.236—0.256%, the nitrogen status would have gone up to values higher than 0.236 or 0.256%. This is a very important matter for improvement of land fertility as a permanent measure all over the world.

#### LAND FERTILITY ACT (1937) OF ENGLAND EFFICACIOUS FOR NITROGEN FIXATION AND PERMANENT AGRICULTURE

In this connection, it is of interest to note that the English people showed a high practical sense when in the famous dairy pastures of Cheshire even 1 ton or more of bone per acre was added to build up the calcium phosphate reserve of land. Moreover, the important step by which the use of lime and basic slag is actually subsidized by the British Government due to the passing of the LAND FERTILITY ACT in 1937, has been all to the good of British Agriculture. Moreover, the American practice of adding N,  $P_2O_5$  and  $K_2O$  in the ratio of 1 : 3 : 2 is certainly more salutary than the European practice of adding these fertilizers in the ratio of 1 : 1 : 1, because, our researches have shown that phosphates help in the nitrogen fixation by organic matter in the course of oxidation. Moreover, we have observed that in phosphate-rich soils even the humus can undergo slow oxidation and fix atmospheric nitrogen and, thus, the C/N ratio of such soils can be smaller than 10. In this way land fertility is increased markedly. Moreover, our researches show clearly that in presence of potassium salts the nitrogen loss in the nitrification of nitrogenous compounds in the soil is minimised.

#### INDIAN BASIC SLAG AS GOOD AS AMERICAN SLAG, AND PROFITABLE FOR CROP PRODUCTION IN CONJUNCTION WITH ORGANIC MATTER

India possesses large amounts of basic slag produced from the expanding steel industry and these slags remain unutilized. From a large number of analysis it has been found that the Tata basic slag contains 7—8% of  $P_2O_5$  which compares favourably with the phosphate content of basic slags in the American markets. The Tata basic slags and other phosphates, when used with organic matter, not only fix atmospheric nitrogen and supply available phosphate and increase the crop production and improve the fertility of normal soils but also reclaim the USAR and alkali soils permanently. The calcium phosphates not only supply the phosphate requirements of human beings, animals, plants and micro-organisms, but, also help the oxidation processes and maintain the neutrality of living cells and tissues.

Continental basic slag usually gives an analysis of 20% total  $P_2O_5$  against Welsh basic slag of 10% total phosphate and American basic slag of 8—10% total  $P_2O_5$ . The old Bessemer slag, with which the famous Cockle Park experiments (Manuring for Mutton) were carried on, contains total phosphorus equivalent to 38—42%, that is 17.4 to 19.2%, tricalcium phosphate with a solubility of 85% by 2% citric acid.

The present Open-Hearth slag of high solubility usually contains phosphorus equivalent to 15—35%, that is 6.8 to 16.0, tricalcium phosphate.



## BASIC SLAG PRODUCES CALCIUM PHOSPHATES BY DECOMPOSING FERRIC AND ALUMINIUM PHOSPHATES IN ACID SOILS

In acid soils and in soils poor in humus, formation of phosphates of Fe, Al and Ti takes place when superphosphate is added to such soils. These freshly formed phosphates of Fe, Al and Ti can undergo hydrolysis and can supply phosphates in small amounts to crops as is evident from our solubility experiments recorded in subsequent pages. Moreover Hester reported that very sparingly soluble ferric and aluminium phosphates can supply appreciable amounts of phosphate to Lima beans, potatoes etc. But, on ageing, these sparingly soluble phosphates become inactive and are not hydrolysed by water or decomposed by carbonic acid. Thus, they become incapable of supplying phosphates to the soil. On the other hand, basic slag which is capable of liberating small amounts of phosphoric acid in the soil, but, has been found to be effective in crop production. The hydrolysis of tricalcium phosphate present in basic slag is checked by the lime present in it. On the other hand, the lime present in basic slag can readily decompose the phosphates of Fe, Al and Ti and can convert them into calcium phosphate which is much readily soluble than phosphates of Fe, Al and Ti. In other words, when basic slag is added to soil, it not only can supply small amounts of phosphoric acid by solution but it becomes a producer of tricalcium phosphate decomposing the sparingly soluble phosphates of Fe, Al and Ti. This is the cause of its efficacy in the soil as a supplier of phosphates.

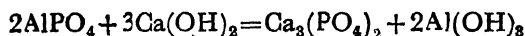
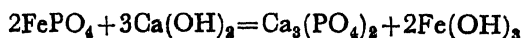
When 1.25 gms. of Tata basic slag containing 8 to 10%  $P_2O_5$  is shaken with 150 c.c. of distilled water for 2 hours and then left to settle overnight at  $20^\circ$ , and filtered next day, 1.43 millimoles of CaO and 0.046 millimoles of  $P_2O_5$  are obtained per litre at  $20^\circ$  whilst a similar experiment carried on with precipitated tricalcium phosphate gives 0.93 millimoles  $P_2O_5$  and 1.08 millimole CaO per litre. In the case of basic slag the hydrolysis of tricalcium phosphate is considerably suppressed by the presence of lime in the slag. That lime is present in the slag and is being dissolved in water when basic slag is shaken with it, is evident from the fact that the amount of dissolved lime in millimoles per litre is 1.43. If tricalcium phosphate exists as such without hydrolysis, the ratio of CaO to  $P_2O_5$  should be 3 to 1. As the amount of  $P_2O_5$  is 0.046 millimoles per litre, the amount of CaO should have been 0.138 millimole, but, the actually observed amount is 1.43 millimole showing a large excess of lime obtainable from the Indian basic slag. On the other hand, the results obtained by Rindell show that in the presence of carbonic acid the amount of CaO in millimoles per litre is 1.9 and that of  $P_2O_5$  is 2.33 millimoles derived from tricalcium phosphate suspended in water containing dissolved carbonic acid whilst with dicalcium phosphate  $CaHPO_4 \cdot 2H_2O$ , the values are 1.67 millimoles CaO and 2.65 millimole  $P_2O_5$  per litre. But with the anhydrous salt  $CaHPO_4$  the values are still smaller, i.e., 0.93 millimole CaO and 1.24 millimole  $P_2O_5$ . These results conclusively prove that carbonic acid and water can break up tricalcium phosphate to a greater extent than dicalcium phosphate which is more stable and exists in solution mainly in the unhydrolysed condition. From the foregoing experimental observations of Rindell, it is quite clear that tricalcium phosphate in contact with water in which  $CO_2$  is dissolved contains very much more phosphate in the dissolved condition than dicalcium phosphate. The lime content in the state of solution from tricalcium phosphate is double of that in anhydrous dicalcium phosphate.

The results obtained by Lachowicz with ferric phosphate suspended in water are very interesting. With water alone the  $P_2O_5$  is 0.046 millimole per litre whilst  $Fe_2O_3$  is 0.023 millimole per litre. In presence of saturated carbonic acid the

values are 0.043 millimole of  $P_2O_5$ , while  $Fe_2O_3$  is 0.023 millimole. With sodium bicarbonate, sodium carbonate, ammonium carbonate and sodium acetate the solubility of phosphoric acid becomes much greater but that of ferric hydroxide becomes smaller than in water.

#### LIME, CHALK, SALTS OF WEAK ACIDS DECOMPOSE FERRIC, ALUMINIUM AND TITANIUM PHOSPHATES

Hence, with ferric phosphate the amount of phosphate in the dissolved condition is about 500th part of that available from tricalcium phosphate and 1/30th of that obtainable from dicalcium phosphate whilst in presence of sodium carbonate the availability of  $P_2O_5$  from ferric phosphate is nearly 45 times greater than in water. Even with  $NaHCO_3$  and  $(NH_4)_2CO_3$  the availability becomes nearly 3.5 times greater. With sodium acetate the availability becomes 2.5 greater. But with carbonic acid there is a slight decrease in the availability. Hence organic manuring of acid soils may not increase the available phosphate in soils. It is well known that ferric hydroxide is a very sparingly soluble substance and is readily formed when  $OH$  ions are available in the system. Lime dissolves appreciably in water and reacts with ferric or aluminium phosphate in the soil according to the equations :—



This is how lime in basic slag breaks up the very sparingly soluble phosphates of iron, aluminium etc. and makes phosphates available to crops. Similarly calcium carbonate can decompose ferric, aluminium and titanium phosphates forming the hydroxides of the metal, carbonic acid and calcium phosphates. Sodium carbonate, bicarbonate, acetate, ammonium carbonate are alkaline due to hydrolysis and produce  $OH$  ions, which can break up the sparingly soluble phosphates and convert them partially into readily soluble phosphates of sodium, ammonium etc. This is the reason of the existence of greater amounts of phosphate in the dissolved condition when ferric or aluminium phosphate is treated with salts of weak acids.

It has been frequently stated that Rothamsted soils are less acidic than Woburn soils, because the calcium carbonate content of Rothamsted soils is of the order of 3.5% to 4%. In Woburn the calcium carbonate is 0.5% or less. Hence in Rothamsted soils the inorganic acid soluble phosphates i.e. phosphates of calcium and magnesium are 20 times greater than in Woburn soils. On the other hand, the inorganic alkali soluble phosphates i.e. phosphates of iron, aluminium and titanium are 10 times greater in Woburn soils than in Rothamsted fields. These experimental results are explained satisfactorily from the above view points discussed in this paper.

#### POSSIBILITY OF LEACHING OF PHOSPHATES FROM SOILS

We have frequently observed that when sparingly soluble phosphates of calcium, magnesium, manganese, zinc, aluminium and iron are vigorously shaken with distilled water at temperatures varying from 20 to 30° for about half an hour, the filtrate after separating the excess of the solid, gives a precipitate of ammonium phosphomolybdate when treated with ammonium molybdate solution and nitric acid. With ferric phosphate a small amount of phosphomolybdate precipitate is obtained whilst with other phosphates which are more soluble larger amounts of

phosphomolybdate can be obtained. All these sparingly soluble phosphate are markedly hydrolysed when treated with distilled water. Moreover, in presence of small amounts of dissolved carbonic acid increased amounts of phosphoric acid are liberated with all the phosphate other than aluminium and iron which appear to be unaffected by the presence of carbonic acid in water. That hydrolysis plays an important part in influencing the amounts of phosphate passing into solution is evident from the following results obtained at 21°, when more phosphate passed into solution with increase of water due to increase of hydrolysis.

1 gram  $P_2O_5$  in the form of different phosphates with different amount of water:—

		200 c.c.	100 c.c.	20 c.c.
		$P_2O_5$ lbs. acre i.e. p. p. m.		
$Ca_3(PO_4)_2$ U. S. A. sample	...	11.1	10.22	4.75
$Ca_3(PO_4)_2$ B. D. H.	„	9.75	9.27	4.67
$CaHPO_4$ Kahlbaum	„	3.15	2.32	2.11
$FePO_4$ B. D. H.	„	2.05	2.05	1.55
$Ca_3(PO_4)_2$ U. S. A. + $CaCO_3$ (0.2 gm)	...		0.7	...

When 3 gms of the phosphate were repeatedly washed with 100 c.c. of boiled distilled water at 25° by shaking for one hour in a mechanical shaker and allowed to stand overnight and then estimated the basic and acidic constituents in the filtrate the following results have been obtained :—

*Tricalcium phosphate*

Washings	pH	Millimoles/litre $P_2O_5$	Millimole/litre CaO	Parts per million parts of water $P_2O_5$	Parts per million parts of water CaO
1	6.06	0.47	1.7	66.6	98.0
2	6.32	0.46	1.3	65.6	73.0
3	6.5	0.46	1.0	64.7	59.0
4	6.66	0.45	0.9	63.0	50.0
5	6.76	0.43	0.85	61.5	48.0
<i>Dicalcium phosphate anhydrous</i>					
1	7.4	0.24	0.51	34.4	29.0
2	7.45	0.18	0.48	25.6	27.0
3	7.5	0.17	0.44	24.6	25.0
4	7.6	0.16	0.42	23.1	24.0
5	7.6	0.16	0.40	22.1	22.0

### Tri magnesium phosphate

1	7.58	1.98	3.4	282	136
2	7.6	1.88	3.1	267	126
3	7.6	1.7	3.0	249	123
4	7.62	1.6	2.9	220	118
5	7.6	1.4	2.9	205	116

### Dimagnesium phosphate

1	7.5	2.17	5.3	308	212
2	7.6	1.8	4.2	258	172
3	7.7	1.6	3.8	225	154
4	7.8	1.4	3.5	198	143
5	7.8	1.3	3.2	191	131

### Aluminium phosphate

1	7.5	0.035	5
2	7.5	0.034	4.8
3	7.56	0.031	4.4
4	7.58	0.03	4.3
5	7.58	0.03	4.2

### Ferric phosphate

1	7.1	0.034	4.8
2	7.2	0.032	4.5
3	7.25	0.03	4.2
4	7.32	0.027	3.8
5	7.36	0.025	3.5

### Tata basic slag

1	8.36	0.005	0.94	0.7	53
2	8.4	0.0045	0.86	0.6	48
3	8.4	0.003	0.7	0.4	39
4	8.42	0.0025	0.6	0.35	33
5	8.46	0.0025	0.52	0.35	29

### Algerian rock phosphate

1	6.7	0.021	0.7	3.0	39
2	6.9	0.017	0.6	2.5	33
3	7.0	0.016	0.41	2.3	23
4	7.15	0.016	0.32	2.2	18
5	7.2	0.016	0.25	2.2	14

### Trichinopoly rock phosphate

1	7.8	0.013	0.6	1.9	33
2	7.8	0.013	0.54	1.8	30
3	7.84	0.012	0.5	1.6	28
4	7.84	0.011	0.46	1.5	26
5	7.88	0.0011	0.44	1.4	25

When calcium phosphates are shaken with water the amount of lime and  $P_2O_5$  passing in solution vary considerably according to the amounts of water taken as is evident in the following results :—

1.25 gms. $Ca_3(PO_4)_2$ + 150 c.c. water	CaO	0.739%
	$P_2O_5$	1.59 %
1.25 gms. $Ca_3(PO_4)_2$ + 50 c.c. water	CaO	0.578%
	$P_2O_5$	0.772%

By shaking at 21° 1.25 grams of different calcium phosphates with 150 c.c. of distilled water for 2 hours and on filtering the contents after 24 hours the following amounts of CaO and  $P_2O_5$  were obtained in millimoles when calculated per litre of the solution :—

Salt	CaO	$P_2O_5$	$P_2O_5$
		mm/litre	p.p.m.
$Ca_3(PO_4)_2$	1.08	0.93	132.5
$CaHPO_4$ anhydrous	0.553	0.24	35.0
$FePO_4$	...	0.092	13.1
$AlPO_4$	...	0.36	52.1

To 1 gram  $P_2O_5$  contents of the phosphates of calcium or iron, 0.2 gr  $CaCO_3$  was added and shaken with 100 c.c. ordinary distilled water for two hours. The filtrates after 24 hours were analysed for their  $P_2O_5$  contents. Similarly on adding 1 and 2 grs of rock phosphate or basic slag to tri and dicalcium phosphate, the experiments were repeated. The following results were obtained :—

$FePO_4$ alone	...	...	.. 0.0041 gr $P_2O_5$
$FePO_4$ + $CaCO_3$	...	...	... 0.00927 gr ,,
$Ca_3(PO_4)_2$ alone	...	...	... 0.0204 gr ,,
$Ca_3(PO_4)_2$ + $CaCO_3$	...	...	... 0.00139 gr ,,
$Ca_3(PO_4)_2$ + 1 gr. rock phosphate	...	...	... 0.0200 gr ,,
$Ca_3(PO_4)_2$ + 2 gr. rock phosphate	...	...	... 0.0184 gr ,,
$Ca_3(PO_4)_2$ + 1 gr. basic slag	...	...	... 0.00024 gr ,,
$Ca_3(PO_4)_2$ + 2 gr. basic slag	...	...	... 0.00014 gr ,,
$CaHPO_4$ Anhydrous alone	...	...	... 0.0062 gr $P_2O_5$
$CaHPO_4$ + $CaCO_3$	...	...	... 0.00008 gr ,,
$CaHPO_4$ + 1 gr rock phosphate	...	...	... 0.005 gr ,,
$CaHPO_4$ + 2 gr rock phosphate	...	...	... 0.0041 gr ,,
$CaHPO_4$ + 1 gr basic slag	...	...	... 0.000064 gr ,,
$CaHPO_4$ + 2 gr basic slag	...	...	... 0.00004 gr ,,

In order to determine what happens when the foregoing experiments are carried on in presence of soil, 0.5 gr  $\text{CaCO}_3$  was mixed with 25 grs normal soil and 0.58 gr  $\text{Ca}_3(\text{PO}_4)_2$  was added to the same mixture. This was shaken with 150 c.c. ordinary distilled water for two hours and the amounts of phosphate in two successive extracts were determined by the photoelectric colorimeter using ammonium molybdate and stannous chloride to develop a blue colour. The following results were obtained :—

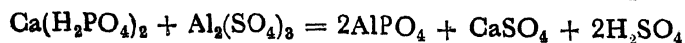
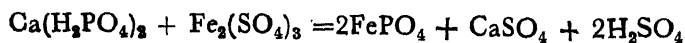
Normal soil alone	First extract traces	Second extract traces
Normal soil + 0.58 gr $\text{Ca}_3(\text{PO}_4)_2$	0.638 mg $\text{P}_2\text{O}_5$	0.438 mg $\text{P}_2\text{O}_5$
“ “ “ + 0.5 gr $\text{CaCO}_3$	0.445 mg $\text{P}_2\text{O}_5$	0.238 mg $\text{P}_2\text{O}_5$
0.58 gr $\text{Ca}(\text{PO}_4)_3$ alone	9 mg $\text{P}_2\text{O}_5$	5.00 mg $\text{P}_2\text{O}_5$

The presence of calcium carbonate checks the hydrolysis of the sparingly soluble phosphates and decreases the washing of  $\text{P}_2\text{O}_5$ . Moreover in presence of soils the washing away of  $\text{P}_2\text{O}_5$  from tricalcium or dicalcium phosphate when treated with water considerably decreases.

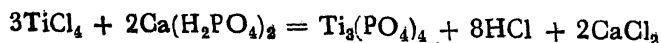
The foregoing results show clearly that the ratio of  $\text{CaO}:\text{P}_2\text{O}_5$  in millimoles in the water extract of precipitated tricalcium phosphate has a tendency to be unity indicating that a solution obtained from treating  $\text{Ca}_3(\text{PO}_4)_2$  by water is really monocalcium phosphate. This has also been observed by Rindell. On the other hand anhydrous dicalcium phosphate passes into water without much hydrolysis. Moreover all the naturally occurring phosphate rocks and the Tata basic slag when shaken with water form a solution much richer in lime than phosphate. This is perhaps due to the fact that all naturally occurring phosphates contain  $\text{CaCO}_3$  varying from 2 to 11 per cent which can suppress the hydrolysis of tricalcium phosphate. The Tata slag contains about 3—5% lime which renders the amount of phosphoric acid passing into solution much smaller than that with tricalcium phosphate alone.

The foregoing experimental observations clearly show that all the sparingly soluble phosphates like tricalcium phosphate, dicalcium phosphate, trimagnesium phosphate, dimagnesium phosphate, even ferric and aluminium phosphates, when treated with water, can yield appreciable amounts of phosphates in the state of solution. The naturally occurring phosphate rocks and basic slag liberate the smallest amount of phosphoric acid in solution.

On the other hand, when superphosphate which is readily soluble is added to acidic soils, the following changes may take place :

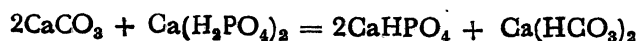


In soils, containing about 1% or less titanium oxide, small amounts of titanium phosphate may also be precipitated as in the equation



The titanium phosphate precipitated is frequently a basic salt that is,  $2\text{TiO}_2 \cdot \text{P}_2\text{O}_5$ .

On the other hand, in soils, rich in calcium carbonate, the following changes take place :—



All these sparingly soluble substances, when freshly formed are more soluble and are more hydrolysed by water than aged varieties of the same compounds present in soil. Consequently more phosphates are available to crops by adding superphosphates or other soluble phosphates to soils. But, when the rainfall is large, there is always the possibility of the leaching of appreciable amounts of phosphoric acid from soils treated with superphosphate. This washing away of phosphates from soils treated with superphosphate seems to be an important factor is causing a low recovery of phosphates in crops. Moreover the gradual formation of fluorapatites and aged ferric, aluminium and titanium phosphates in the soil leads to a marked decreased in the phosphate liberation in the system and a low availability by crops.

It is interesting to record here that G. W. Robinson and J. O. Jones reported a marked washing of phosphates in the wet soils of Wales where the rainfall is large. Moreover, K. Iverson has recently reported that the loss of phosphate from average mineral and organic soils of Denmark in areas of average rainfall varies from 0.4 to 3.6 kilograms of  $\text{P}_2\text{O}_5$  per hectare. Hall pointed out that the Rothamsted surface soils lose one kilogram of phosphoric acid per acre per year by leaching. Some workers have reported losses from sandy soils and others from soils, receiving heavy phosphate treatment. Serious losses of phosphates take place with much run off water.

In the following table the phosphate position of some Rothamsted soils and the phosphate washability has been recorded :—

Complete analysis of soil	$\text{P}_2\text{O}_5$ %	Water extracts of soil	
		$\text{P}_2\text{O}_5$ p. p. m.	$\text{P}_2\text{O}_5$ lbs/acre
Unmanured	0.099	0.525	0.59
N+K <sub>2</sub> O	0.102	0.808	0.90
N+P <sub>2</sub> O <sub>5</sub>	0.173	3.900	4.36
N+K <sub>2</sub> O+P <sub>2</sub> O <sub>5</sub>	0.183	4.025	4.50
Farmyard manure	0.176	4.463	5.00

In U. S. A. the following results were obtained :—

$\text{P}_2\text{O}_5$  extracted from surface soils by oil pressure method.

Soils	$\text{P}_2\text{O}_5$ p. p. m.	$\text{P}_2\text{O}_5$ lbs/acre
Fine sandy loam	3.7	4.14
Medium sandy loam	5.2	5.80
Glyde fine sandy loam	4.0	4.46
Miami silt loam	12.2	13.50
Peat	15.6	17.40

In manured rotational plots, manured cereal plots, unmanured rotational plots, and unmanured cereal plots the water soluble  $P_2O_5$  was 44.9 lbs, 8.77 lb, 4.4 lbs and 4.39 lbs per acre respectively. It has been reported that ordinary cultivated fields of U. S. A. seldom lose more than 10 lbs of  $P_2O_5$  per acre. In well water or irrigation water small amounts of  $P_2O_5$  are obtained. Similarly in saline and alkaline solution the phosphate content is very low. Soils having 6.7 to 7.4 pH lose 0.55 lbs.  $P_2O_5$  when the rainfall is 51 inches. By applying 2 tons of  $CaCO_3$  in the form of chalk or basic slag the amount of phosphate washed decreases with chalk but increases when basic slag was added.

In our experiments when a good soil containing 0.4%  $P_2O_5$  and 4.1%  $CaO$  is shaken with distilled water at  $25^\circ$  for 2 hours, the loss of phosphate is as follows with different amounts of water per unit weight of soil :-

	Soil water ratios						
	1 : 2	1 : 3	1 : 5	1 : 10	1 : 25	1 : 50	1 : 100
Lbs/acre $P_2O_5$ lost per washing	6.2	7.5	7.5	8.0	30.0	51.96	93.2

A soil much poorer in phosphate i.e. 0.079%  $P_2O_5$  and containing 1%  $CaO$  similarly washed with distilled water loses  $P_2O_5$  in lbs/acre as follows :-

	Soil water ratios		
	1:2	1:10	1:25
Lbs/acre $P_2O_5$ lost per washing ...	0.25	0.57	0.75

In our experiments, a sample of Ganges sand containing 0.47%  $CaO$  and 0.078%  $P_2O_5$  when shaken with water and sand in the ratio of 2 parts of water to 1 part of sand, 0.64 lbs. of  $P_2O_5$  per acre was washed away. In general phosphate rich soils lose more  $P_2O_5$  by leaching than phosphate poor soils.

It is interesting that with an Indian soil containing 0.4%  $P_2O_5$  and 4.1%  $CaO$  the washing with distilled water in the ratio 1:2.5, was 6.8 lbs.  $P_2O_5$ /acre, whilst in Rothamsted which has a rainfall of 25 inches per year, the amount of phosphate washed in the soil receiving farmyard manure and containing 0.176%  $P_2O_5$ , is approximately 5 lbs.  $P_2O_5$ /acre. The pH of our soil is slightly on the alkaline side. The Rothamsted soil is rich in calcium carbonate, i.e. to the extent of about 3.5% contains chiefly  $CaHPO_4$  and  $Ca_3(PO_4)_2$ . Consequently with a rainfall of 25 inches which is equivalent to soil to water ratio of 1:2.5, the washability of phosphate is of the same order as that of a good quality Indian soil.

In our experiments we have definitely shown, that phosphates check the loss of lime. Similarly calcium carbonate or lime present in a soil or added to it, suppresses the hydrolysis of the sparingly soluble phosphates and preserves them in the soil. There is no doubt that lime and phosphate help each other in maintaining their status in soils.

It has been reported in U. S. A. that the areas of soil richest in phosphorus occur in the limestone belt of Kentucky where the soils are known to contain well over 10000 lbs per acre and those lands are fertile and maintain their fertility for a long time. Arrhenius has observed that soils near human habitations, past or present in different parts of Sweden and Java are richest in phosphate and fertile. Similar results have been recorded in the neighbourhood of cities in Denmark.



Hinkle showed by chemical analysis that calcareous soils are well supplied with total phosphorus but available phosphate was small. Recent results from Idaho University indicates that though there is reduction in available phosphorus when phosphate fertilizer is applied to calcareous soil, the succeeding crops utilise a great deal of fixed phosphate. Hence P-fixation is not so marked in calcareous soils. Collins reports that most nutritious pastures in England and best dairy pastures in France are those that are rich in phosphates. All these facts support the view that calcium carbonate and phosphate conserve each other and that the phosphate status of soils determines their fertility level as postulated by Dhar.

#### RECOVERY OF PHOSPHATES

In a previous paper, it has been stated that generally the recovery of phosphates in experiments carried in North-West Europe, does not exceeds 40% but usually it is less. Similarly the recovery with Gafsa mineral phosphate is stated to be 29%, with a high soluble basic slag, the recovery can go upto 40%. In Cockle Park, Northumberland, England, 200 lbs of phosphoric acid in the form of basic slag was added first followed by 100 lbs after 3 years. The soil of Cockle Park is a heavy clay, well limed and contained 0.034 to 0.121% total  $P_2O_5$ , but was deficient in available phosphate. It was reported that in Cockle Park, the recovery was as follows :—

	Tree field
$P_2O_5$ applied per acre since 1897	... 1200 lb.
Recovered in live weight increase	... 8 %
Found in top 9 inches of soil	... 91 %

Moreover, Russell has stated that after the recovery of 25 to 30% of the phosphate added in experiments in Britain, there is no evidence that the remaining 70 to 75% of the phosphate can ever be recovered.

On the other hand, Lohnis & Fred have reported the following recovery in field experiments, lasting for 4 years.

Nitrogen	$P_2O_5$	$K_2O$
7.8 to 46.1%	10.1 to 75.6%	22.4 to 85.1%

The above results show that under favourable conditions, the recovery of phosphate can be much higher than that of nitrogen. For a number of years we have studied the problem of nitrogen loss and we have proved that nitrogen is lost from soils not only by leaching but there is considerable loss of nitrogen in the gaseous state due to the formation and decomposition of the unstable substance ammonium nitrite in the nitrification of all types of nitrogenous compounds. Consequently the recovery of nitrogen hardly exceeds 50% even under most favourable conditions. In agriculture, all over the world, by adding ammonium sulphate or urea, the recovery is usually 25%.

Even when soluble phosphates are added to soils, sparingly soluble phosphates are formed, but these sparingly soluble phosphates being freshly formed are more soluble and more hydrolysed than the aged materials present in the soil. Consequently addition of soluble phosphates to soils not only help crop production as has been reported all over the world, but it is also responsible for its low recovery due to leaching by rain water, specially where the rainfall is heavy.

This has been reported by Robinson and Jones in experiments carried on in Wales where the rainfall is high. Also very sparingly soluble fluorapatites, ferric, aluminium and titanium phosphates are formed in acidic soils on adding soluble phosphates. These do not yield appreciable  $P_2O_5$  due to ageing. On the other hand, by adding basic slag, although the amount of soluble phosphoric acid is low, there is always the formation of tricalcium and dicalcium phosphates by the action of lime present in basic slag on the phosphates of Fe, Al and Ti. Moreover, due to the presence of organic matter undergoing slow oxidation in the soil more available phosphate is produced by the interaction of carbonic acid, nitric and nitrous acids and perhaps weak organic acids formed in the soil. In this process, dicalcium phosphate and small amounts of monocalcium phosphate may be formed which can supply phosphates to crops growing in land treated with basic slag. Similarly soft phosphate rocks containing small amounts of fluorine mixed with organic substances are certainly suitable in permanent agriculture. Grasses grow abundantly on lands treated with Tata basic slag.

In Germany, there is a saying, that lime makes the father rich but the son is impoverished by liming the field. This has been interpreted in Europe by assuming that lime helps in the conversion of humus into nitrate, and other plant food materials into soluble condition. In presence of lime the velocity of oxidation of humus becomes quick, the loss is quick and hence the son obtains a land of which the humus is lost a good deal. Agriculturists all over Europe have always used dung in large doses in maintaining the fertility. As a matter of fact the only manure used was dung and lime before the 20th Century in Europe. Now this is a fairly good combination as the dung is a complete manure containing in 10 tons, 135 lbs.  $CaO$ . Moreover, there is phosphate and potash and nitrogen and trace elements in dung.

From our researches, we are convinced that dung or straw or green manure or grass when mixed with finely divided soft phosphate rock or basic slag can fix larger amounts of atmospheric nitrogen, than a mixture of dung and chalk and supply available nitrogen, phosphate and potash. It is well known that basic slag is less alkaline than calcium carbonate i.e. weight for weight, the alkalinity of basic slag is approximately half to  $\frac{2}{3}$ rd of that of lime. Similarly, finely divided rock phosphate is less alkaline than calcium carbonate. Hence these materials when added to soils liberate nitrate from humus at a lower speed than calcium carbonate. Thus the application of finely divided rock phosphate or specially basic slag mixed with organic substances is certainly more profitable than dung and chalk as has been done in Europe so far. From our researches, we are convinced that basic slag, which is being produced in India as well as other parts of the world in increasing amounts, when incorporated with dung or green manure or straw or grass or water hyacinth or Municipal wastes and ploughed in the soil is going to increase land fertility considerably and maintain its neutrality and is going to help permanent agriculture all over the world.

That phosphate and organic matter is beneficial has been supported by Lady Eve Balfour of the Soil Association, New Bells farm, Haughley, Stowmarket, Suffolk, England, in the following lines :—

“...I was extremely interested in your views concerning the use of finely ground natural rock-phosphate in composts, dung, etc. I am a great believer in the value of powdered rock material and also in the superiority of the calcium compounds over the various other more usual fertilizer forms of phosphates and other minerals.

On certain soils I would go so far as to say that the use of ground rock of

this kind was an absolutely essential part of organic farming. This is especially true on leached soils such as occur on the Eastern side of the United States.

In the near future we shall be reviewing, in consultation with a number of scientists, the outcome of the last five years' work here and our future programme, including possible modifications, and when you are next in England I hope you will give us the opportunity of discussing it all with you".

*Influence of light on nitrogen fixation by Azotobacter*

It has already been emphasised that in our experiments on nitrogen fixation by different energy materials, the amount of nitrogen fixed in milligram per gram of carbon oxidized is always greater in presence of light than in the dark, although the number of Azotobacter is invariably smaller in light than in the dark.

We have also studied the influence of light on nitrogen fixation by Azotobacter culture media.

100 c.c. of the following nitrogen free Beijerinck (1901) medium

Tap water	...	one litre
Mannitol	...	20 grams
K <sub>2</sub> HPO <sub>4</sub>	...	0.2 gram

was sterilized, inoculated with 1 gram of fertile garden soil and incubated at 25° to 30°. After a few days a thin grey pellicle was formed on the surface, which, later on became thick and brownish black. An examination of the pellicle revealed typical Azotobacter cells i.e. diplococci or short rods with slimy capsules. Transfers were effected by inoculating the freshly sterilized cultures with a part of the pellicle. In this manner, several transfers were carried on till a fairly pure enriched culture of Azotobacter was obtained.

Experiments on the influence of light on nitrogen fixation were carried on with these Azotobacter cultures.

**Experiment No. 1.**

500 cc. of the following medium

Mannitol	20 grams.
K <sub>2</sub> HPO <sub>4</sub>	0.2 gram.
CaCO <sub>3</sub>	10 grams.
Tap water	one litre

were taken in two 750 cc. pyrex glass flasks, sterilized and inoculated with the fairly pure culture of Azotobacter. One flask was wrapped up with thick black cloth to cut off light. Both the flasks were exposed to sun light from May 20, 1949 to October 24, 1949 for 150 days. After this exposure to sun light, the culture medium exposed to sun light looked whitish, whilst the covered one appeared yellow containing brownish flaky material. In the exposed medium, a few Azotobacter cells were visible, but the covered flask contained numerous diplococci,

An aliquot portion of the culture was evaporated with a drop of dilute sulphuric acid and analysed for total organic carbon and nitrogen. The following results were obtained :—

Treatment	Organic carbon introduced grams	Organic carbon recovered grams	Total nitrogen obtained milli-grams	Efficiency i.e. amount of nitrogen fixed in milligram per gram of carbon oxidized
Light	3.817	1.3965	20.87	8.6
Dark	3.817	1.4115	17.50	7.3

#### Experiment No. 2

Flasks containing 400 c.c. of the sterile medium already described was again inoculated with fairly pure cultures of *Azotobacter* and one flask was exposed to sunlight and another was covered with thick black cloth and put in the sun along with the exposed one for different periods. The following results were obtained :—

Exposed to sun light from 25-2-50 to 16-4-50

Treatment	Organic carbon introduced grams	Organic carbon recovered grams	Total nitrogen obtained milligrams	Efficiency i.e. amount of nitrogen fixed per gram of carbon oxidized
Light	3.084	2.856	4.25	18.6
Dark	3.084	2.404	8.50	12.5

Exposed to sun light from 10-11-49 to 15-1-50

Light	3.054	1.032	25.0	12.4
Dark	3.054	0.8857	24.0	11.0

Exposed to sun light from 10-11-49 to 18-2-50

Light	3.054	0.8799	19.75	9.1
Dark	3.054	1.0434	16.00	8.0

The nitrogen obtained in the systems is caused by the fixation of atmospheric nitrogen, as there was no nitrogen which can be estimated in the original culture.

The foregoing results clearly indicate that when the system is exposed to sun light for about 2 months or less, the oxidation of carbon in the dark sets may be higher than in the exposed ones. But when the exposure to sun light is for longer periods, the oxidation of carbon is greater in light than in the dark. The amount

of nitrogen fixed in milligram per gram of carbon oxidized is always greater in light than in the dark in all the sets. This is certainly due to the fact that the light energy is actually absorbed by the system containing calcium carbonate and Azotobacter cells and is utilized in fixing additional amounts of nitrogen than in the media not receiving sunshine. It is apparent that under natural conditions in the soil containing organic matter and Azotobacter marked photochemical fixation of the atmospheric nitrogen takes place on the soil surface by absorption of light energy.

#### *Studies on phosphorylation*

We are carrying on a very large number of experiments on the physical properties of mixtures of phosphoric acid with different carbohydrates, amino acids and other nitrogenous compounds in order to throw light on the problem of phosphorylation. We have recently carried on experiments on the lowering of freezing point and electric conductivity measurements of phosphoric acid solutions containing different concentrations of cane sugar. We have determined the viscosity and electric conductivity of such solutions at 30°. These measurements have been compared with those obtained with lactic acid and cane sugar. The experimental results are recorded in the following tables.

#### *Experiments with Phosphoric acid.*

##### Depression of freezing point.

Freezing Point Beckman Thermometer reading			Lowering of Freezing Point.
Water	...	4.66	...
M/2 Phosphoric acid	...	3.562	1.098°C
M/2 H <sub>3</sub> PO <sub>4</sub> + M/2 Sucrose...		2.393	2.267°C
M/2 H <sub>3</sub> PO <sub>4</sub> + M Sucrose	...	1.173	3.487°C
M/2 H <sub>3</sub> PO <sub>4</sub> + 3M/2 sucrose		-0.15	4.81°C
Molar phosphoric acid	...	2.34	2.32°C
M H <sub>3</sub> PO <sub>4</sub> + M/2 Sucrose	...	1.08	3.58°C
M H <sub>3</sub> PO <sub>4</sub> + M Sucrose	...	-0.19	4.85°C

Composition of Mixture	Depression observed	Depression calculated
M/2 Acid + M/2 Sucrose	2.267°C	2.118°C
M/2 Acid + M Sucrose	3.487°C	2.958°C
M/2 Acid + 3M/2 Sucrose	4.81°C	3.888°C
M Acid + M/2 Sucrose	3.58°C	3.25°C
M Acid + M Sucrose	4.85°C	4.18°C

*Electric conductivity measurements at 30°*

	Molar conductivity	Viscosity	Corrected conductivity	Density
M/5 $\text{H}_3\text{PO}_4$	86.5 ohm <sup>-1</sup>	1.062	91.85 ohm <sup>-1</sup>	1.01
M/2 $\text{H}_3\text{PO}_4$	67.54 ohm <sup>-1</sup>	1.117	75.44 ohm <sup>-1</sup>	1.026
M $\text{H}_3\text{PO}_4$	59.12 ohm <sup>-1</sup>	1.23	72.71 ohm <sup>-1</sup>	1.049
M/5 $\text{H}_3\text{PO}_4$ + M Sucrose	35.25 ohm <sup>-1</sup>	2.883	101.60 ohm <sup>-1</sup>	1.138
M/2 $\text{H}_3\text{PO}_4$ + M Sucrose	25.40 ohm <sup>-1</sup>	2.994	76.17 ohm <sup>-1</sup>	1.153
M $\text{H}_3\text{PO}_4$ + M Sucrose	21.74 ohm <sup>-1</sup>	3.48	75.67 ohm <sup>-1</sup>	1.173

*Experiments with lactic acid.*

Depression of Freezing point.

	Freezing point Beckman thermometer reading	Lowering of Freezing point
Water	4.68	...
M/2 Lactic acid	3.65	1.03
M/2 Acid + M/4 Sucrose	3.11	1.57
M/2 Acid + M/2 Sucrose	2.49	2.18
M/2 Acid + M Sucrose	1.13	3.55
M/4 Lactic acid	4.17	0.51
M/4 Acid + M Sucrose	1.91	2.77

Electric conductivity at 30°.

Liquid	Molar conductivity	Viscosity	Corrected Molar conductivity
M/5 Lactic acid	15.26 ohms <sup>-1</sup>	1.033	15.75
M/2 „ „	9.132 „	1.126	10.28
M „ „	5.619 „	1.219	6.84
M/5 Acid + M sucrose	6.695 „	2.308	15.45
M/2 Acid + M sucrose	4.032 „	2.491	10.02
M Acid + M sucrose	2.392 „	3.021	7.226

The foregoing results clearly show that when phosphoric acid is mixed with cane sugar, the freezing point of the mixture is appreciably greater than the cal-

culated value. This shows that in presence of cane sugar, phosphoric acid forms a complex acid which apparently is more ionised and stronger than phosphoric acid itself. This conclusion is also supported by molecular conductivity measurements, which when corrected for viscosity changes are greater with mixtures than with phosphoric acid alone. With lactic acid and cane sugar the formation of complex compounds producing stronger acids seem much less pronounced than with phosphoric acid. In our experiments with acetic, propionic, butyric acid etc. with cane sugar, the molecular conductivity of the mixtures even when corrected for viscosity changes, shows smaller values than with the organic acids themselves.

## SUMMARY

1. The significant facts are that the phosphate contents of the skeletal remains of (a) mammals, birds, fishes, reptiles, amphibia, etc. vary only from 16 to 18.5%, (b) the phosphorus content of normal human serum varies from 5.6 to 3.75 milligrams per one hundred c. c. of serum and (c) the phosphate contents of bacteria and fungi are high.

2. The phosphate contents of crops are smaller than their nitrogen and potash contents.

3. Leaves of forest trees contain less phosphates than wheat or oat straw.

4. The North African phosphates and those of South Eastern part of U.S.A. are believed to be sedimentary deposits obtained from the sea bottom. They are usually soft and suitable for direct application to soils for crop production. Similarly phosphated lime stones formed by the action of guano on chalk deposits, are suitable for direct application.

5. As sea water contains much more fluorine than phosphorus, the calcium phosphates obtained from the plant and animal life in sea, which is a vast source of natural calcium phosphates are always associated with calcium fluoride. The reactivity and solubility of natural phosphates generally decrease as the fluorine content increases.

6. U. S. A. is specially strong and U. S. S. R. is next in possessing natural phosphate deposits. West Europe has to depend on U. S. S. R. and North Africa for phosphates. Asia has no status in phosphate reserves.

7. Experimental results show that a Swedish clay soil containing 0.147% total nitrogen when mixed with sucrose (1.5% carbon) undergoing slow oxidation in air gains in nitrogen which attains the value of 0.168% in light and 0.1598% in the dark. In presence of a Gafsa phosphate rock contributing 0.25%  $P_2O_5$  to the system the total nitrogen goes up to 0.1992% in light and 0.1658% in the dark.

8. When a sample of Allahabad soil containing 0.042% total nitrogen is mixed with sucrose (1.5% carbon) which is being oxidised, the nitrogen content increases to 0.0675% in light and 0.0521% in the dark. When Tata basic slag containing 8%  $P_2O_5$  is added to the system to the extent of 0.25%  $P_2O_5$ , the nitrogen increases to 0.0960% i.e. an increase of 250% in light. In the dark the nitrogen becomes 0.0546%. Other phosphates are found to increase nitrogen fixation markedly.

9. Cowdung when mixed with the same soil fixes nitrogen appreciably. The efficiency of nitrogen fixation i.e. the amount of nitrogen fixed in mgms per gram of carbon oxidised, has the value 27.5 in light and 16 in the dark. In presence of

Bihar rock phosphate yielding 0.25%  $P_2O_5$ , the efficiency becomes 56 in light and 25 in the dark.

10. In presence of phosphates the nitrogen fixation by straw in presence of light has an efficiency of 38% while with sugar candy the efficiency is 25%. Hence the efficiency of this type of nitrogen fixation by the slow oxidation of organic matter by air in presence of phosphates in light can be three times greater than the Haber-Bosch or the cyanamide method of fixing atmospheric nitrogen and is of the same order as in legumes.

11. By adding three different doses of cowdung in three years the total nitrogen content of a soil containing 0.037% nitrogen rose to 0.2%.

12. Municipal wastes mixed with bones when incorporated with Allahabad soil containing 0.04% nitrogen, raised the total nitrogen to 0.25%. In presence of basic slag in some cases the nitrogen content was further elevated to 0.33%. Grasses grow very well on lands treated with Tata basic slag.

13. Finely divided lignite or Assam coal when mixed with normal or alkali soil undergoes slow oxidation and fixes atmospheric nitrogen both in light and in dark. The efficiency in normal soil with lignite is 15 in light and 9 in dark. With Assam coal, the efficiency is 16.4 in light and 9.8 in dark. With alkali soil and lignite the efficiency is 8.8 in light and 4.9 in dark. With Assam coal in alkali soil the efficiency values are 10.6 and 5.8. In presence of phosphates the efficiency markedly increases.

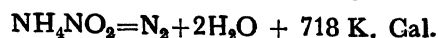
14. Experimental results show that in composting of all types of organic substances, addition of finely divided phosphates or basic slags fixes atmospheric nitrogen appreciably in composts and increases their fertilizing value.

15. Straw when mixed with water and kept at 35° for three months, fixes nitrogen markedly.

16. Calcium phosphate rich soils containing humus when allowed to undergo slow oxidation in air, markedly increases in total nitrogen due to fixation of atmospheric nitrogen. Hence the carbon-nitrogen ratio of such soils is smaller than 10.

17. Calcium phosphate markedly retards the loss of nitrogen, as nitrogen gas in the nitrification of ammonium sulphate.

18. Loss of nitrogen in the gaseous state is always associated with the nitrification of all types of nitrogenous compounds, as in the oxidation of ammonia and its compounds. This is due to the formation and decomposition of the unstable substance, ammonium nitrite, according to the equation :



Ammonium nitrite is always formed as an intermediate product in the oxidation of ammonia or ammonium salts or amino acids or proteins forming nitrates.

19. By adding about 100 lbs of nitrogen per acre as ammonium sulphate or sodium nitrate to soils, the soil humus undergoes loss in temperate countries.

20. Rothamsted results as summarised by Russell clearly indicate soil deterioration when fertilized by ammonium sulphate or sodium nitrate, not only in continuous cropping but in rotations as well and that only farm yard manure markedly increases land fertility even in continuous cropping. Moreover, the yield of barley and wheat in Rothamsted experiments was greater and more steady with farm yard manure than with artificials. On adding farm yard manure, the total



nitrogen of the fields increased from 0.122 to 0.256% and this increase of nitrogen and humus leads to the steady liberation of greater amounts of available N, K, P and trace elements causing greater crop yields.

21. Our experimental results have clearly established that not only farm yard manure but cow dung and dung of other animals, molasses, sugars, starch, glycerol, cellulose, lignin, oils, fats, straw, grasses water hyacinth, leaves, peat, lignite, finely divided bituminous coal etc., when mixed with soil undergo slow oxidation with liberation of energy which fixes atmospheric nitrogen, more in light than in the dark. In this process, light energy is actually utilized in fixing greater amounts of nitrogen than in the dark, because the chemical energy obtained from the oxidation of energy materials and light energy obtained either from the sun or artificial sources, are utilized in this type of nitrogen fixation.

22. Large amounts of nitrogen are fixed on the soil surface by the catalytic, photochemical and bacterial oxidation of organic matter produced by photosynthesis.

23. Hence all kinds of organic matter which can undergo slow oxidation in soil in air can improve the nitrogen status and increase land fertility markedly. This has been observed all over the world. This type of nitrogen fixation is the chief source of nitrogen supply to world crops.

24. A large number of experiments carried on in this laboratory show clearly that all kinds of calcium phosphates, finely divided phosphate rocks and basic slags increase markedly this type of nitrogen fixation both in light and in the dark, because phosphates stabilise proteins in soils.

25. All over the world phosphate rich soils are generally found to be rich in humus and in total nitrogen.

26. Bad alkali soils have been permanently reclaimed by treating them with mixtures of organic substances like sunhemp, *Dhaincha*, clover, straw, dilute molasses mixed with calcium phosphates or basic slags. Excellent results have been obtained in laboratory experiments as well as in field trials.

27. Experimental results show that sparingly soluble tricalcium phosphate, dicalcium phosphate, trimagnesium phosphate, dimagnesium phosphate when shaken with water liberate appreciable amounts of phosphoric acid in the solution. In presence of carbonic acid more phosphoric acid is liberated, but in presence of lime or calcium carbonate, the phosphoric acid liberation becomes less.

28. Similarly finely divided phosphate rocks, basic slag, ferric phosphate, when treated with water gives out small amounts of phosphoric acid. In presence of carbonic acid with basic slag and rock phosphate, there is increased liberation of phosphoric acid, but with ferric phosphate, there is no increase of phosphoric acid, but with alkaline substances like lime, chalk, sodium carbonate, bicarbonate, acetate, there is increased liberation of phosphoric acid from ferric phosphates.

29. Hence liming of acidic soils or adding basic slag helps in increased liberation of calcium phosphate and thus the phosphate recovery by crops is improved.

30. Experimental results show that  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  when treated with water produces more  $\text{P}_2\text{O}_5$  than  $\text{Ca}_3(\text{PO}_4)_2$ , which in its turn liberates more  $\text{P}_2\text{O}_5$  than anhydrous  $\text{CaHPO}_4$ . In soils containing humus and free carbonic acid  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is likely to be formed when basic slag or finely divided rock phosphate

phate is added to soils. Soft phosphate rocks containing very small amounts of fluorine formed by the phosphating of lime stones are most suitable as a phosphatic manure for direct addition to soil; because these are decomposed by water and carbonic acid more than hard varieties rich in fluorine.

When superphosphate or other soluble phosphate is added to ordinary soils containing lime  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Ca}_3(\text{PO}_4)_2$  are formed. In acidic soils without lime very sparingly soluble phosphates of Fe, Al & Ti are likely to be produced along with acids. Hence, the lime requirements of acidic soils increase and in soils rich in calcium carbonate, the lime requirement decreases on adding superphosphate.

31. It has been reported in Europe that the recovery of phosphate is low. This seems to be due to the formation of fluorapatites, aged ferric phosphates, aluminium phosphates and titanium phosphates which yield very small amount of phosphates in rain water. Moreover, in soils containing calcium carbonates, the calcium and magnesium phosphates are likely to predominate and they are leached appreciably.

32. The recovery of phosphates under favourable conditions should always be greater than that of nitrogenous compounds.

33. Basic slag and chalk are valuable specially in acidic soils because of their ability to decompose very sparingly soluble phosphates of Fe, Al, Ti forming more soluble calcium phosphates.

34. Phosphates check the loss of lime by leaching from soils and calcium carbonate decrease the hydrolysis of all sparingly soluble phosphates and thus checks the loss of phosphates by leaching in soils when heavy rains fall.

35. Because the calcium carbonate content of Rothamsted Soils is approximately 8—10 times greater than in Woburn Soils, the phosphates of Ca and Mg are 20 times greater in Rothamsted Soils than in Woburn. The phosphates of Fe, Al and Ti are 10 times greater in Woburn than in Rothamsted Soils.

36. The formation of natural nitre beds in arid regions seems to be influenced by the fixation of atmospheric nitrogen from the oxidation of sea weeds and other organic substances aided by natural calcium phosphate deposits which protect the nitrogenous compounds from loss in the process of nitrification and help in the production of nitrates under natural conditions.

37. Experimental results show that the carbonaceous compounds in water hyacinth (*Eichhornia*) which is rich in potash and total nitrogen, when mixed with soil, undergo oxidation with liberation of energy. This chemical energy of oxidation of the carbonaceous compounds present in water hyacinth, is actually utilized in fixing atmospheric nitrogen in soil even in the dark. When the system is exposed to light, light energy is absorbed and the nitrogen fixation is increased by utilizing the light absorbed. When basic slag is also added to the soil-water hyacinth system, the nitrogen fixation both in light and in dark is markedly increased. Hence a mixture of water hyacinth and basic slag is highly suitable for increase of crop production.

38. A mixture of organic substances like dung, farm yard manure, straw, leaves, water hyacinth etc. with bone meal or finely divided soft phosphate rocks or basic slag can lead to soil conservation and increase of land fertility by accentuation of the humus content of soil. This method is as effective as the growing of legumes.

39. It is estimated that  $365 \times 22$  million K. Calories of Solar energy fall per acre of land per year but only a small part of this solar energy is utilized in crop production or fixation of atmospheric nitrogen on the soil surface along with the fixation of nitrogen taking place by absorption of chemical energy obtained in the oxidation of carbohydrates, celluloses, lignin and other energy materials.

40. Experimental results obtained in different parts of the world show that finely divided soft phosphate rocks is almost as effective in crop production as basic slag. All these sparingly soluble neutral and alkaline sources of phosphate have more residual effect than superphosphate or other soluble phosphates.

41. Experimental results show that when a sterile culture medium containing mannitol,  $K_2HPO_4$ ,  $CaCO_3$  and tap water inoculated with a fairly pure culture of Azotobacter is exposed to sunlight and another set covered with thick black cloth is placed next to the exposed one, the amount of nitrogen fixed per gram of carbon oxidized, is always greater in light than in the dark. This is due to the fact that the light absorbed by the media is actually utilized in fixing atmospheric nitrogen even in the system containing Azotobacter cells.

42. In our studies on the problem of phosphorylation we have experimentally observed that the lowering of the freezing point of aqueous solutions of phosphoric acid with cane sugar is greater than the calculated values. This observation can be explained from the view point that a mixture of cane sugar and phosphoric acid forms a complex acid stronger than phosphoric acid. Electrical conductivity of the same mixture when corrected for viscosity changes is appreciably greater than phosphoric acid alone and this measurement supports the view point of the formation of an acid appreciably stronger than phosphoric acid when this acid is mixed with cane sugar.

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